# THE ALUMINUM PHOSPHATE ZONE OF THE BONE VALLEY FORMATION, FLORIDA, AND ITS URANIUM DEPOSITS

By ZALMAN S. ALTSCHULER, ELIZABETH B. JAFFE, and FRANK CUTTITTA, U. S. Geological Survey

## CONTENTS

## ILLUSTRATIONS

## TABLE

### ABSTRACT

The Bone Valley formation of Pliocene age, which contains most of the land-pebble phosphates, occurs in west-central Florida, east of the Tampa Bay region. It unconformably overlies the Hawthorn formation of early and middle Miocene age and is covered by a surface mantle of quartz sands. It contains graded bedded pebbly and clayey phosphatic sands in its lower two-thirds, which are mined, and a less phosphatic massive-bedded clayey sand, approximately 8–10 feet thick, in its upper third, which is discarded.

The upper part of the Bone Valley formation has been leached, altered to aluminum phosphates, and enriched in uranium in a widespread though discontinuous zone which averages about 6–7 feet in thickness and underlies several hundred square miles of the Peace and Alafia drainage basins. The areal distribution patterns with respect to the thickness, tonnage, and grade of the aluminum phosphate zone conform strikingly to the topography of the river valleys.

The Bone Valley formation was altered by weathering and ground water, and the vertical changes through the aluminum phosphate zone show a progressive change in mineralogy and texture. In typical sections carbonate-fluorapatite still prevails at the base, incipiently leached and altered. In the middle of the zone, the calcium aluminum phosphates crandallite and millisite are found, and at the top the aluminum phosphate wavellite predominates. The changes have been brought about by phosphatization of clay and by alumina alteration of apatite.

Much apatite and clay have been leached and replaced in the aluminum phosphate zone, and its rock is generally white, friable, and highly porous; however, its character has been greatly influenced by the primary Bone Valley petrography. Thus, where graded bedded pebbly rock is altered, coarse, frequently graded, vesicularity results; where massive clayey sand is altered, fine porosity prevails, and aluminum phosphates are more common.

The uranium content of unaltered rock of the lower part of the Bone Valley is approximately 0.008 percent; its $P_2O_5$ content is about 15 percent. Unaltered rock of the upper part of the Bone Valley contains much less uranium and $P_2O_5$. By contrast, a well-developed section of aluminum phosphate zone typically has 0.012 percent uranium and approximately 8–10 percent $P_2O_5$. Within the aluminum phosphate zone, uranium increases as calcium does, and the more calcic phosphates are more uraniferous. In addition, supergene processes have caused a subzone of basal enrichment in the aluminum phosphate zone in which individual apatite specimens contain as much as 0.X percent uranium. Except for a single trace occurrence of autunite, no uranium minerals have been found in the Bone Valley formation.

The aluminum phosphate zone is a potentially valuable resource of uranium, phosphate, and alumina, particularly as it

495

must be stripped anyway to mine the underlying apatite deposits, and its rock can be readily beneficiated by removal of quartz, the major diluent.

## INTRODUCTION

In the upper part of the Bone Valley formation, Florida, a discontinuous zone of alteration containing aluminum phosphate overlies the commercially mined apatite which constitutes the land-pebble phosphates. This aluminum phosphate zone has been known for many years. In 1949, however, during the U. S. Geological Survey's exploration studies for uranium, it was found to be fairly widespread and enriched in uranium; this greatly enhances its value as a potential resource, not alone of uranium but also of alumina and phosphate. The aluminum phosphate desposits result from the lateritic alteration of the Bone Valley formation by ground water and represent the progressive replacement of clay and apatite in a paragenetic sequence which has recently been reported from other similarly altered phosphate deposits—those of Nigeria (Russ, 1924) and Sénégal (Capdecomme, 1953). Thus, in addition to its economic interest, the aluminum phosphate zone is intrinsically interesting to the geologist because it represents a general type of alteration in the particular petrogenetic domain of phosphorites.

Much of the work reported here was originally published in an administrative report to the U. S. Atomic Energy Commission in December 1949. The authors are much indebted to associates in the U. S. Geological Survey for more recent contributions to their efforts: to J. P. Owens and R. M. Berman for X-ray investigations of pseudowavellite and millisite, to E. J. Young for field and laboratory studies on the genesis and distribution of zones of weathering and surficial deposits; to J. B. Cathcart, the highlights of whose economic studies have been freely drawn on, and to C. B. Hunt for his stimulating guidance and criticism in many of the field problems.

### GENERAL GEOLOGY AND STRATIGRAPHY

The Bone Valley formation of Pliocene age (Cathcart and others, 1953) underlies 2,600 square miles in west-central peninsular Florida, east of the Tampa Bay region, in Polk and Hillsboro Counties and extending into adjoining counties (fig. 171). The region is generally flat and exposures are limited to the phosphate mines and to a few spots in the banks of the Alafia and Peace Rivers, which drain the area. A low north-trending ridge of subdued karst topography divides the Peace and Alafia drainages in the center of the region. The Bone Valley unconformably overlies the Hawthorn formation of early and middle Miocene age

(MacNeil, 1947) and is covered by a mantle of loose quartz sand.

The Hawthorn formation consists mainly of quartzose and slightly phosphatic limestone and marl. Its upper part has been irregularly altered to dolomite; and its clay, normally montmorillonite, has been transformed to attapulgite. The Hawthorn's surface is irregular, its rock is solution pitted, and it contains many small slumps, and locally large ones, within which the overlying Bone Valley thickens (Cathcart, 1950). In addition the Bone Valley strata drape over irregularities of the Hawthorn surface, owing to postdepositional solution and slumping. Probably the Hawthorn was exposed and weathered during late Miocene time, forming an irregular karst topography and accumulations of phosphatic residuum consisting of primary apatite nodules and secondary phosphatized limestone pebbles. Marine transgression during the Pliocene dolomitized the weathered limestone and reworked the clastic residuum and phosphatized limestone into the Bone Valley formation, at the same time adding unknown amounts of quartz, clay, and phosphate. Later uplift, continuing in the Recent, induced new subterranean solution and slumping, and is responsible for the present karst topography.

The Bone Valley formation is a pebbly and clayey sand of quartz and phosphate. Much of its clastic material is transgressively reworked residue of the Hawthorn. The formation is normally 25–30 feet thick and is characteristically graded bedded in its lower two-thirds, which is the pebbly phase that is mined and known commercially as matrix (fig. 172). The materials in the graded bedded phase range from pebbly sand through sand, clayey sand, and clay. In the upper third of the Bone Valley, the graded bedded deposits change rapidly to massive-bedded clayey quartz sand containing only minor amounts of clastic phosphate. This upper zone and the overlying quartz sand are discarded as overburden during mining.

The Bone Valley is composed of approximately equal amounts of quartz, clay, and phosphate minerals. Their distribution is uneven, however, because the upper part of the Bone Valley is 60–70 percent quartz sand in a groundmass of clayey cement, and the lower part of the Bone Valley is correspondingly higher in phosphate particles and lower in quartz.

The phosphate in Hawthorn and unaltered rock of the Bone Valley occurs primarily as nodules and pebbles of carbonate-fluorapatite (Altschuler and others, 1953). The clay in the lower part of the Bone Valley is an iron-rich montmorillonite, and in the upper, massive-bedded Bone Valley it is a kaolinite. The change from montmorillonite to kaolinite is a postdepositional alteration and does not conform precisely to the
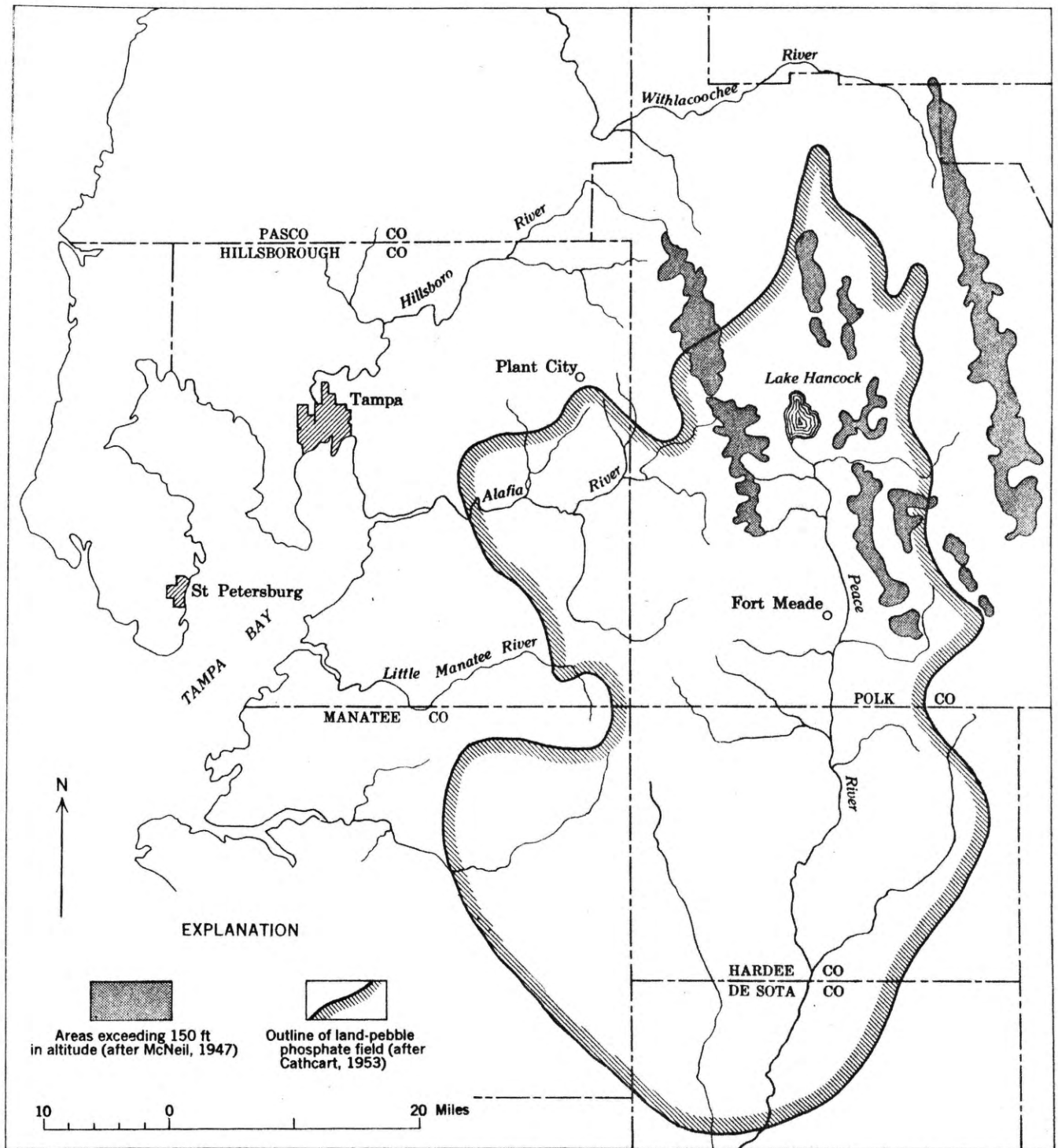
FIGURE 171.—Map of west-central Florida showing the outline of the land-pebble phosphate field.   Shaded areas are belts of ridgeland enclosed by 150-foot contour.

boundary between the upper and lower units of the Bone Valley.

Generally the Bone Valley formation is compact although not indurated, and it is gray or greenish gray owing to the ever-present clay.  In places red-brown or orange is superimposed irregularly by oxidative weathering of clay.  In the mines of the Peace and Alafia drainage basins, a white zone of leaching and alteration irregularly transgresses the upper part of the section (fig. 172).   This is the aluminum phosphate zone.  Its rock is vesicular, friable, light in weight, and composed of quartz sand that is cemented and indurated by the secondary minerals wavellite, crandallite, and, locally, millisite.   In the aluminum phosphate

EXPLANATION

Quartz sand

Leached and vesicular rock
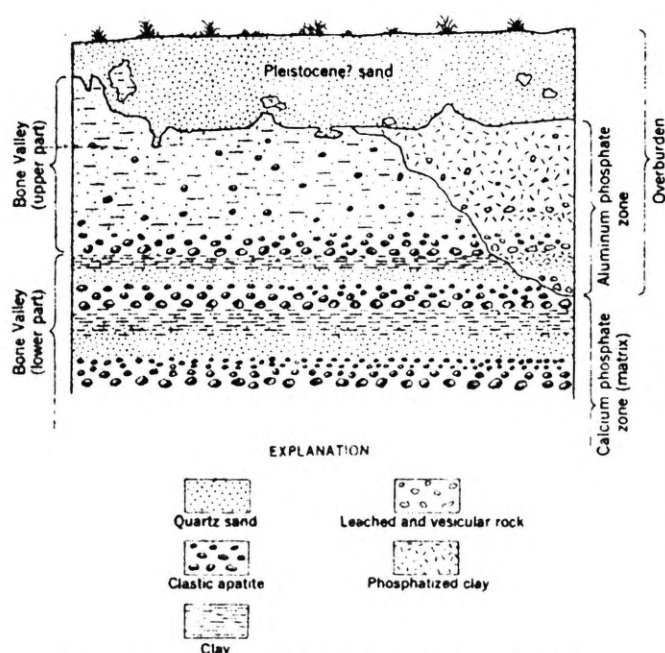
Clastic apatite

Phosphatized clay

Clay

FIGURE 172.—Stratigraphic relations in the aluminum phosphate zone.

zone, therefore, the lithology of the section as previously outlined has been modified by leaching, secondary precipitation, and replacement. These modifications, as well as the chemical characteristics and uranium contents of the rock, depend greatly on whether only the upper or both of the primary lithologic zones of the Bone Valley formation have been altered. Thus, coarsely vesicular rock is confined to originally pebbly strata (fig. 172); and because these were the apatite-rich layers, the calcium aluminum phosphates crandallite and millisite are abundant in such rock. Where the alteration is restricted to the upper part of the Bone Valley, however, the aluminum phosphate wavellite is the dominant mineral, the porosity is more uniform, and the rock is finely vesicular.

Secondary precipitates underlie the aluminum phosphate zone in irregular, discontinuous seams of hardpan which cement layers of sand and encrust upper surfaces of clay. The cement consists of dark apatite and, subordinately, of limonite and chert. The chert represents silica released during the phosphatization of clay to wavellite and crandallite. Seams of silica can be seen closely associated with clay in process of such alteration higher in the section. The hardpans are formed by material leached from above and redeposited at the ground-water table during the early stages of leaching; hence, apatite, rather than secondary phosphate, prevails.

Pebbles of apatite at the base of the leached zone record the onset of alteration. They are softened, highly porous, and rimmed by a bleached and whitened zone of crandallite and wavellite. Within the next 2

feet the pebbles are completely altered and white, and, finally, cavities occur that are comparable in size and sorting to the pebbles in the adjoining rock. Where the leaching is most intense, holes coalesce, and all parts of the rock are affected. Higher in the section, uniformly porous phosphatic sandstone prevails where the rock was originally well-sorted clayey sand.
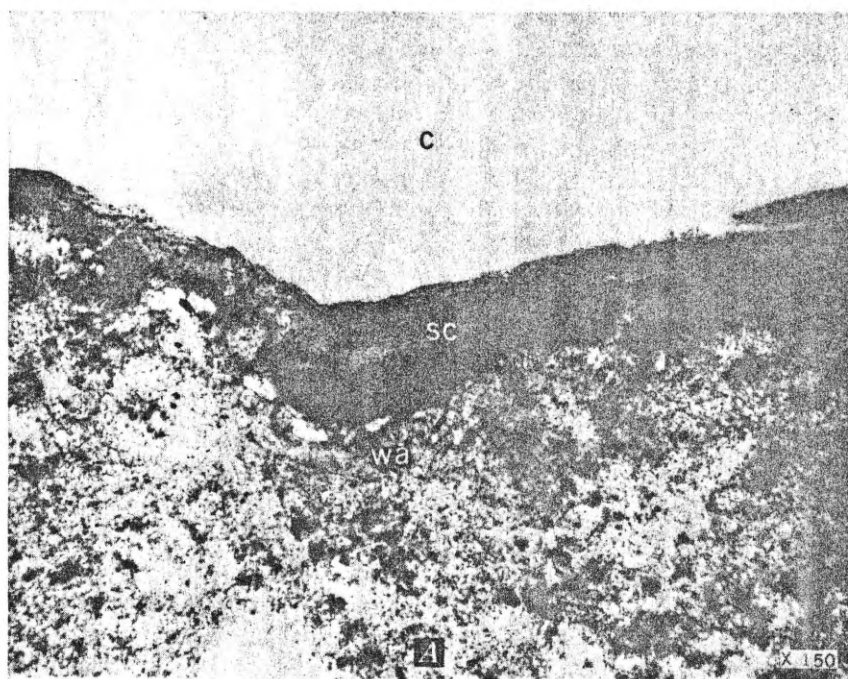
Another important modification within the aluminum phosphate zone is the fine-grained secondary cement that coats most fractures and cavities (pl. 11). Much of it is layered and built up from the floors of the cavities in concave, lenslike masses that are devoid of silt. The secondary cement is a mixture of kaolinite, apatite, and aluminum phosphates. Its habit implies deposition from descending solutions from which phosphate minerals were precipitated; kaolinite, either reforming from solution or carried in suspension, was deposited synchronously. From bottom to top of the section, the composition of the secondary cements shows the same change from calcium to aluminum phosphates as does the zone as a whole. Thus, apatite drops out as crandallite and wavellite become successively predominant. Microscopic examination reveals wavellite needles discordantly replacing the previously deposited mixtures, thus representing not merely the precipitation of a later phase but progressive alteration (pl. 11).

The precipitation of secondary cement is dependent both on degree of leaching and stratigraphic position. At the base of the aluminum phosphate zone, cavity fillings are microscopic and secondary cements occur only as fracture fillings and coatings around partly leached grains. In the middle of the zone where leaching is more pronounced, secondary cements may constitute 10 percent of the rock, mainly in the form of layered cavity fillings. Toward the top of the section, leaching has been most pronounced; however, eluviation predominates and secondary cements diminish again. In the uppermost few inches a sharp increase in cement content underlies the boundary with the loose sands and probably represents a caliche deposited during occasional periods of desiccation.

## DESCRIPTIVE MINERALOGY

The principle minerals of the aluminum phosphate zone are apatite, crandallite, millisite, and wavellite. Of these, crandallite and wavellite are the most typical, because apatite is generally confined to the basal part of the zone and millisite is important only locally.

*Carbonate-fluorapatite.*—The fine-grained apatite in the aluminum phosphate zone, like that in the rest of the Bone Valley formation and other marine phosphorites, is characterized by a deficiency in $P_2O_5$ content of 3–6 percent, an excess of F or $(F+OH)_2$ of 0.5–1 percent, and the presence of approximately 3 percent of

UNCROSSED NICOLS



CROSSED NICOLS

**WAVELLITE REPLACING FINE-GRAINED APATITE (wa) AND SECONDARY CEMENT (sc) LINING THE BOTTOM OF THE CAVITY (c).**

carbonate (Altschuler and others, 1953; Jacob and others, 1933). In addition, the apatite is demonstrably smaller in unit-cell dimensions than igneous fluorapatite (Altschuler and others, 1953). The structural differences revealed by the characteristically smaller cell dimensions are best explained by the chemical deviations, which can be expressed in the formula $Ca_{10}(PO_4CO_3)_6F_{2-3}$.

The apatite always occurs as aggregates of submicroscopic crystals. Its index of refraction ranges from 1.575 to 1.625 and is typically about 1.605. It is generally isotropic, but fibrous varieties show birefringence of about 0.003, positive elongation, and parallel extinction. The specific gravity of the pure apatite nodules is 2.96–2.99.

*Crandallite* [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$].—Crandallite (Palache and others, 1951) in the aluminum phosphate zone is entirely secondary. It replaces either apatite or kaolinite and is intimately mixed with them. It inherits their fine-grained textures and is predominantly isotropic. It may also be associated with the secondary minerals, millisite, wavellite, and goethite. Depending on the amount of intermixed minerals, the index of refraction of crandallite ranges from 1.590 to 1.630. Purest varieties are least birefringent and have an index of 1.615. Crandallite is white to pale gray in reflected light and colorless to brown in transmitted light. The composition of crandallite departs from the ideal formula in having 11–12 percent CaO instead of 13.55. The specific gravity of this crandallite is approximately 2.75–2.78.

*Millisite* [$(NaK)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O$].—Millisite (Palache and others, 1951) is known to occur as a major component of the aluminum phosphate zone within one area of several square miles and is present only in minor or trace amounts elsewhere. Like crandallite, with which it occurs as a microcrystalline intergrowth, millisite is fine grained and virtually isotropic. The presence of millisite was demonstrated in X-ray studies of J. P. Owens and R. Berman, of the Geological Survey. Its mass index refraction is 1.630, and it is pale greenish white. The specific gravity of millisite in the aluminum phosphate zone is the same as that of crandallite.

Millisite requires alkalies; hence, its restricted ocurrence, in contrast to crandallite, is probably related to the distribution of montmorillonite. In most areas montmorillonite had been transformed to kaolinite before the phosphatization of clay, and crandallite developed in preference to millisite.

*Wavellite* [$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$].—Wavellite (Palache and others, 1951) occurs in the aluminum phosphate zone in two ways: as bands of cryptocrystalline fibrous material of low birefringence, index of refraction of 1.580, and as euhedral white bladed crystals, crystal aggregates, and spherulites. The euhedral material is most common and can be readily identified by its optical properties and mode of occurrence. Its indices of refraction are $\alpha$ 1.52–1.53, $\beta$ 1.535, and $\gamma$ 1.546. Its specific gravity is between 2.30 and 2.33. The wavellite occurs as druses and vein fillings, as spherules in cavities, or replacing clay and apatite (pl. 11). The cryptocrystalline variety is primarily a clay replacement.

## PETROLOGY

The nature of the alteration in the aluminum phosphate zone is shown in table 1, a series of chemical analyses from the Homeland mine of the Virginia-Carolina Chemical Corp., at Homeland, Fla. These samples are representative of the thickest section of the aluminum phosphate zone in figure 172. Sample Ho–20 is from the basal part of the zone, and Ho–25 is a sample of the uppermost material. Quartz and clay as reflected by $SiO_2$ content are higher on the average in the upper part of the section; and CaO, $CO_2$, and F, all of which reflect apatite, drop off sharply from bottom to top. The relative changes are shown in figure 173 where the major oxides are recomputed and plotted on a silica-free basis according to their stratigraphic position. As very little clay remains in this particular section, this is equivalent to removal of quartz, which being relatively inert, is unaffected by the alteration.

It can be seen in figure 173A that CaO and $Al_2O_3$ have a complementary relation in the aluminum phosphate zone but that $P_2O_5$ shows a slight, though steady decline toward the top of the section, reflecting general leaching of phosphate minerals. The abrupt drop in $P_2O_5$ in sample Ho–22 and the corresponding peak in $Al_2O_3$ are due to the presence of kaolinite in an originally thick clay layer. Otherwise, the respective upward and downward trends of the $Al_2O_3$ and CaO curves correspond almost exactly to a gradual replacement of apatite (3.3 CaO:1 $P_2O_5$) by crandallite and wavellite (both 3 $Al_2O_3$: 2 $P_2O_5$). Thus, $Al_2O_3$ increases half as rapidly as CaO falls, because $Al_2O_3$ in crandallite and wavellite requires about twice as much $P_2O_5$ as does CaO in apatite.

The reversal of trend in CaO content in the uppermost material (Ho–25) results from the aforementioned increase of secondary cement containing crandallite. An increase merely in the amount of cement might represent only textural control or material introduced from above during last stages of weathering. However the concomitant increase in calcium phosphate content indicates transport of material from below and deposition by evaporation, particularly as calcium phosphate has disappeared in several feet of subjacent section.

The mineral composition at Homeland is reflected in the ratios of CaO to $P_2O_5$ and $Al_2O_3$ to $P_2O_5$ in figure

173*B*. Apatite is not found in any samples above Ho–21. Crandallite is a major mineral only in sample Ho–21 and Ho–22. From this point to the top of the section crandallite is of minor importance, and the ratio of CaO to $P_2O_5$ declines sharply above Ho–21 and remains small thereafter. Wavellite is a major component throughout the section, and the ratio of $Al_2O_3$ to $P_2O_5$ is large initially and increases upward.

Experiments by Warrenton, cited by A. L. DuToit (1917), have shown that calcium phosphates in the presence of carbonated water can be dissolved by aluminum hydroxides with the formation of aluminum phosphates. Laboratory and soil fertilization studies indicate that clays may be transformed to calcium aluminum and aluminum-phosphates in acid conditions. Field and microscope evidence for such reactions in the aluminum phosphate zone have been described above, namely, the progressive replacement of clays and apatite by crandallite and wavellite and the occurrence of chert seams adjacent to wavellitized clay. We may state that these reactions proceed from the top of the section downward and are still incomplete at the base. This is evident from the vertical sequence. Thus, the most acid phase, wavellite, dominates at the top; and the less stable, more basic phases, crandallite and apatite, are successively more dominant downward. also, wavellite needles can be seen replacing earlier deposited secondary cements at the base.

## URANIUM DISTRIBUTION IN THE ALUMINUM PHOSPHATE ZONE

The uranium in the Bone Valley formation, and indeed in most other phosphorites, is associated intimately and almost entirely with the phosphate minerals. In 1949 a single trace occurrence of autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$, was found by the authors in the aluminum phosphate zone, and C. Arambourg and J. Orcel (1951) and A. A. Guntz (1952) have reported trace occurrences of torbernite-group minerals in Morocacn phosphates. These occurrences are quantitatively insignificant. In laboratory experiments uranium is not differentially leached from apatite or aluminum phosphate rock with complexing or noncomplexing acids. Further, the clay, quartz, carbonate, and other minerals associated with apatite in phosphorites always contain less than 0.001 percent uranium.

Unaltered phosphorite in the lower part of the Bone Valley formation averages 0.008 percent uranium and contains 10–15 percent $P_2O_5$. Unaltered clayey sand from the upper part of the Bone Valley contains only minor amounts of $P_2O_5$ and approximately 0.002–0.003 percent uranium. In contrast, typical rock from well-formed sections of the aluminum phosphate zone has 8–12 percent $P_2O_5$ and approximately 0.012 percent

uranium. Furthermore, the rock in the aluminum phosphate zone generally contains 60–70 percent quartz and 5–10 percent kaolinite, both relatively non-uraniferous diluents. The aluminum phosphate zone has thus had twofold to fourfold enrichment in uranium, even in contrast to the matrix.

Although there is much and expectable difference in the composition and uranium content of the aluminum phosphate zone, the distribution of uranium within it generally exhibits the pattern illustrated in figure 173 and reflects the mineral, chemical, and stratigraphic relations. As shown in figure 173*A*, the uranium content increases sharply just above the base of the zone, declines gradually in the middle, and is relatively low in the upper half. Moreover the distributions of uranium and lime are strikingly similar. Analyses of pebbles, cements, and mineral concentrates for uranium show that the apatite pebbles are the most enriched of the aluminum phosphate zone components and that the pebbles in the base of the zone are richer than those in the middle. Individual pebbles from the base of the zone commonly have tenths of a percent of uranium, although pebbles from the same strata outside the zone of alteration contain only 0.02 percent of uranium. Concentrates of crandallite and millisite generally contain 0.03–0.04 percent uranium. In contrast, pure wavellite contains only 0.002–0.004 percent uranium. Despite the low uranium content of wavellite, the upper part of the aluminum phosphate zone (table 1 and fig. 173*A*) generally contains about 0.01 percent uranium; however, this is attributable to minor amounts of crandallite.

Thus, uranium associates most strongly with the more calcic phases, preferentially with apatite. When apatite is depleted uranium is enriched in crandallite. This is clearly demonstrated by the virtually identical curves for uranium and $CaO/P_2O_5$ (fig. 173*B*) for samples Ho–20 to Ho–22. Ho–22 is the first sample in which apatite is missing, and the $CaO/P_2O_5$ drops accordingly as the remaining lime is fixed in crandallite. At this point the uranium curve abruptly departs from the $CaO/P_2O_5$ curve although it generally parallels its trend through the remainder of the section.

The correspondence between CaO and uranium and the basal enrichment of uranium in apatite suggest that uranium substitutes for calcium in the apatite structure. This is plausible on crystallochemical grounds because the ionic radii of quadrivalent uranium (1.05A) and bivalent calcium (1.06A) (Goldschmidt, 1954) are virtually identical, and both V. E. McKelvey and J. M. Nelson (1950) and V. M. Goldschmidt (1954) have proposed the substitution. Recent work (Altschuler and others, 1954) demonstrating that much of the uranium in apatite is quadrivalent essentially

TABLE 1.—*Chemical analyses of seven samples from the aluminum phosphate zone*

[Anlayst, F. Cuttitta]

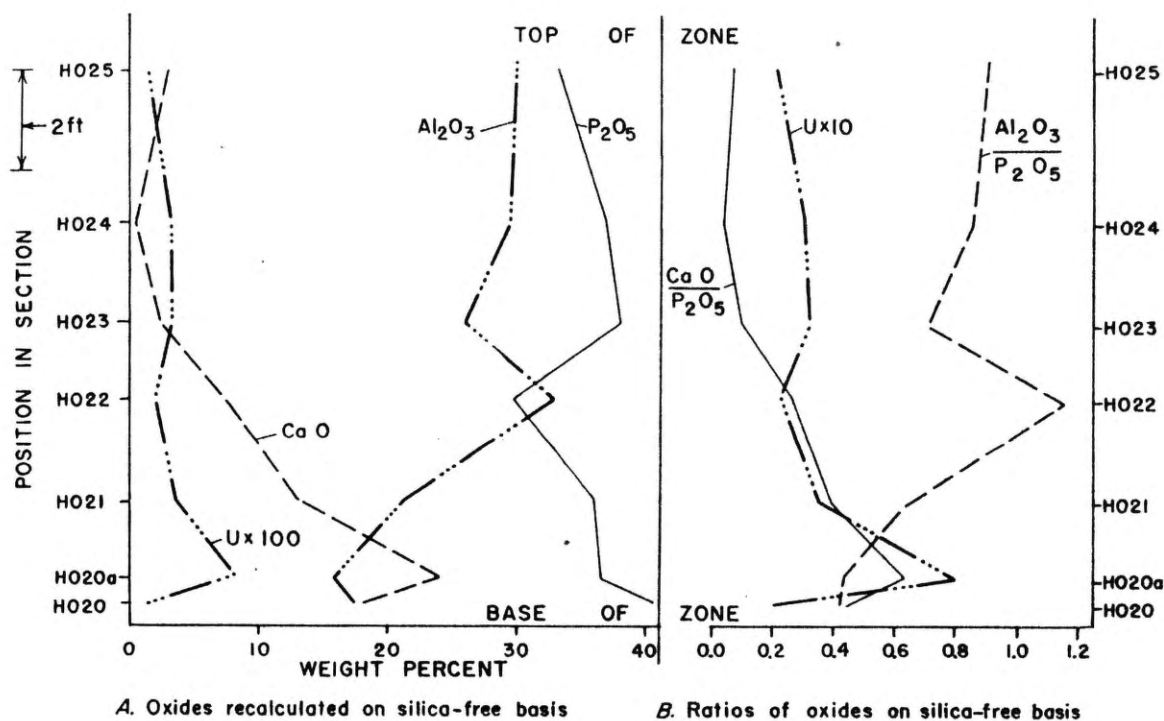| Constituent | Ho-20 | Ho-20A | Ho-21 | Ho-22 | Ho-23 | Ho-24 | Ho-25 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 51. 48 | 62. 60 | 40. 92 | 57. 24 | 69. 46 | 68. 08 | 51. 32 |
| $Al_2O_3$ | 8. 26 | 5. 98 | 12. 48 | 14. 17 | 8. 16 | 9. 40 | 14. 91 |
| $Fe_2O_3$ [a] | 2. 76 | 2. 86 | 2. 61 | 2. 17 | 1. 32 | 1. 33 | 2. 19 |
| MnO | . 70 | . 53 | 2. 14 | . 16 | . 16 | . 14 | . 13 |
| MgO | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 |
| CaO | 8. 98 | 8. 25 | 8. 00 | 3. 10 | . 90 | . 20 | 1. 20 |
| $Na_2O$ | . 23 | . 13 | . 12 | . 15 | . 06 | . 04 | . 03 |
| $K_2O$ | . 00 | . 00 | . 00 | . 00 | . 00 | . 00 | . 00 |
| $TiO_2$ | . 37 | . 40 | . 63 | . 63 | . 31 | . 42 | . 65 |
| $P_2O_5$ | 19. 72 | 13. 60 | 20. 79 | 12. 79 | 11. 61 | 11. 32 | 16. 35 |
| Loss on ignition [b] | 6. 76 | 6. 09 | 11. 72 | 9. 96 | 7. 91 | 9. 18 | 13. 24 |
| $CO_2$ | . 80 | . 24 | . 26 | . 05 | . 02 | . 02 | . 05 |
| F | 1. 15 | . 52 | . 63 | . 59 | . 51 | . 70 | . 53 |
| Cl | . 03 | . 02 | . 04 | . 01 | . 03 | . 02 | . 01 |
| $SO_3$ [c] | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 |
| $Cr_2O_3$ | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 | . 01 |
| $V_2O_5$ | . 00 | . 00 | . 00 | . 00 | . 00 | . 00 | . 00 |
| U [d] | . 01 | . 03 | . 02 | . 01 | . 01 | . 01 | . 01 |
| Total | 101. 28 | 101. 28 | 100. 39 | 101. 06 | 100. 49 | 100. 89 | 100. 65 |
| Less F=O | . 48 | . 22 | . 27 | . 25 | . 22 | . 30 | . 22 |
| Less Cl=O | . 01 | . 01 | . 01 | . 00 | . 01 | . 01 | . 00 |
| Corrected total | 100. 79 | 101. 05 | 100. 11 | 100. 81 | 100. 26 | 100. 58 | 100. 43 |
| $H_2O$—(110°C) | . 35 | . 49 | 1. 13 | . 64 | . 73 | . 39 | . 88 |

[a] This represents total iron, some of which may be present as ferrous iron.
[b] The figures for loss on ignition include adsorbed water ($H_2O$–) and exclude $CO_2$.
[c] This represents total sulfur; no sulfides were found.
[d] Uranium is reported as a metal, as its valence state was not determined.



A. Oxides recalculated on silica-free basis    B. Ratios of oxides on silica-free basis

FIGURE 173.—Chemical differences in the aluminum phosphate zone related to stratigraphy.   A, oxides recalculated on silica-free basis; B, ratios of oxides on silica-free basis.

establishes the proof. Considering that uranium occurs in apatite in amounts of one atom per several thousand unit cells, the excess charge involved in the substitution of uranium for calcium can easily be balanced by a number of substitutions known to occur in apatite or by excess fluorine. The replacements of calcium by sodium and of phosphate by silicate are both of far greater magnitude than the replacement of calcium by uranium. The sexivalent uranium in apatite can usually be explained by postdepositional weathering or by oxidation incident to radioactive decay. Thus a mechanism is supplied for explaining the zone of basal enrichment within the aluminum phosphate zone. The amount and manner of enrichment in the entire zone are discussed below.

## ORIGIN OF THE ALUMINUM PHOSPHATE ZONE AND ITS URANIUM ENRICHMENT

The following are the distinctive features of the aluminum phosphate zone: (1) It transgresses the stratigraphy and always extends downward from the top of the Bone Valley formation, (2) it is commonly underlain by hardpans reflecting old ground-water levels, (3) its mineralogic and textural changes progress vertically through the section and diminish downward, and (4) it is characterized by leaching and reprecipitation involving the depletion of CaO, $Na_2O$, silicate silica, and some phosphate, and the complementary increase in $Al_2O_3$, coordinated as acid aluminum phosphates which yield downward to basic calcium phosphates.

This combination of features implies postdepositional lateritic alteration by acid ground water. It also implies downward percolation controlled by the ground-water table. The ground water of the region was probably rich in humic "acids" derived from soils, bogs, and ground-water podzols of Pleistocene age; "fossil" and current examples of these occur in the area. One of the first changes in the alteration sequence is the transformation of montmorillonite to kaolinite. Thus, although the unaltered clayey sand is kaolinitic, the change from montmorillonite to kaolinite transgressed the primary stratigraphic horizon separating pebbly graded beds from massive clayey sands. Moreover, minor amounts of montmorillonite are found in many sections of the kaolinitic clayey sand, and discrete residual patches of montmorillonite containing appreciable apatite sand have been found in one section of otherwise fresh-looking kaolinitic sand containing only minor amounts of apatite.

Coincident with the alteration of montmorillonite to kaolinite, or shortly thereafter, clay and apatite were dissolved, and the phosphoric acid thus generated reacted with clay to produce crandallite and wavellite.

Aluminum hydroxides reacted with apatite and also produced crandallite and wavellite. Further, crandallite was precipitated as a secondary cement from acid solutions which percolated downward and were neutralized in the more basic zone containing apatite. During early stages of leaching, calcium was more abundant, and crandallite was the main secondary phase. With additional acid-ground-water percolation, the more stable end product (wavellite) gradually replaces the intermediate phase (crandallite).

The picture of downward leaching and redeposition accords well with the pattern of uranium distribution. Uranium is liberated during the leaching of apatite pebbles in the upper part of the zone. It is kept soluble in the descending acid waters, probably as complexed uranyl and uranous ions, and it is secondarily enriched (Altschuler and others, 1954) in the porous partly leached apatite pebbles at the base of the zone by structural replacement of calcium. Work by C. F. Baes, Jr., (1954) demonstrates that sexivalent uranium can be reduced to quadrivalent uranium by the oxidation of ferrous iron in acid solutions and that this reaction is furthered by the presence of fluorine and phosphate. Thus, even under oxidizing conditions some low-valence uranium could persist after release from apatite and be available for uptake in the manner proposed. It is necessary to postulate the presence of the uranyl ion because of the thermodynamic relations favoring the transformation of $U^{4+}$ to $UO_2^{++}$ (Garrels, 1955) and also because of the trace occurrence of autunite which indicates local concentration of $UO_2^{++}$.

Presumably only low-valence uranium would be fixed by diadochy, and uranium could also be adsorbed by apatite as uranyl phosphate. Experimental evidence has shown that apatite can fix appreciable uranyl ion (Neuman and others, 1949; Moore, 1954). Valence analysis of the uranium in apatite from the base of the leached zone has shown that the ratio of quadrivalent to sexivalent uranium is lower than in comparable unenriched apatite; however, the total amount of quadrivalent uranium may be higher. This indicates that the apatite in the aluminum phosphate zone may have taken up both uranous and uranyl ions. It is equally possible that the initial uptake was largely of uranous ion and that continual weathering and decomposition of the host apatite have caused oxidation to the uranyl state.

The mode of occurrence of uranium in crandallite and wavellite is not known. It is assumed to be intimately associated as uranyl phosphate. The downward secondary enrichment of uranium is based on the properties of the entire aluminum phosphate zone, however, and applies equally to these minerals. L. Capdecomme

and R. Pulou (1954) also report uraniferous crandallite deposits that are more radioactive in the basal zone.

The presented theory of supergene enrichment of uranium demands the original presence of 2 or 3 times more apatite than now occurs in the aluminum phosphate zone. Although the initial content of apatite in the zone was undoubtedly higher than the amount remaining, it is not possible to assume a twofold to threefold increase in percent of apatite in view of the primary stratigraphic change to a less phosphatic clayey sand that can be observed in relatively unaltered outcrops. It is known from field and laboratory evidence, however, than an originally thicker section was available for leaching of apatite to provide the present enrichment in uranium. Briefly, the contacts between the loose sands and the upper part of the Bone Valley are gradational in detail, and the sands of both zones are virtually identical in size, sorting, and heavy-mineral content. Therefore, part of the loose sand mantle is a blanket of lateritically weathered and eluviated upper part of the Bone Valley and hence not a Pleistocene deposit, and the present contact is a lowered one.

J. B. Cathcart mapped the regional occurrence of the aluminum phosphate zone and established that its isopach and isograde contours generally conform to the topography of the river valleys. The zone is thickest and richest in uranium under the outer slopes of the flood plains, and the changes in grade and thickness of the zone migrate upstream in most of the tributaries and toward the master streams on all the interfluves in the manner of topographic contours.

The degree of accord between equivalent uranium and chemically determined uranium in the aluminum phosphate zone indicates that the zone and its distribution and grade patterns originated in Pleistocene time and are probably preglacial. Precise ages cannot be proposed at this time.

The relation of the aluminum phosphate zone both to the ground-water table and to the stream valleys indicates that the weathering and leaching are related to stream incision and a lowering of the ground-water table, probably caused by slight regional uplift during Pleistocene time. The downcutting and the adjustment in the ground-water system would have been most pronounced in the lower reaches of the rivers, and the resultant ground-water leaching and deposition are therefore most profound on the slopes of the master-stream valleys. The formation of postdepositional subterranean solution caves and their collapse reflect the present topography, cause supratenuous folding in the Bone Valley, and are related to this initial uplift as well as to later movement.

## ECONOMIC GEOLOGY

The aluminum phosphate zone underlies several hundred square miles in the valleys of the Peace and Alafia Rivers, and it averages 6–7 feet in thickness. Known reserves exceed 800 million tons according to V. E. McKelvey (and others, 1953). Several million tons of aluminum phosphate zone rock are stripped annually in mining the calcium phosphate deposits. The aluminum phosphate zone generally averages 0.01–0.02 percent uranium and is therefore a potential source of tens of thousands of tons of uranium.

The average content of phosphate minerals in the aluminum phosphate zone is 20–30 percent. The potential reserves of alumina and phosphates with which uranium is associated are thus hundreds of millions of tons.

Certain petrographic features of the aluminum phosphate zone are, particularly auspicious for economic exploitation. The rock is a friable phosphatic sandstone. More than 60 percent of the rock is quartz that is coarser than 150 mesh (0.1 mm). Virtually all of the phosphatic material is finer than the quartz or can be reduced to finer size during disaggregation. Thus, by a separation into appropriate coarse and fine fractions, a twofold to threefold concentration of the phosphate, alumina, and uranium can be obtained with moderately high recovery. Furthermore, because of its characteristic basal enrichment in uranium, the aluminum phosphate zone can be easily delimited in prospecting by shallow radioactivity logging.

In view of the auspices under which these discussions are assembled, it is appropriate to emphasize not only the inherent geologic interest of the aluminum phosphate zone but also the benefits that would result from its utilization. The added stimulus of great quantities of recoverable uranium makes possible the exploitation of vast deposits of alumina and phosphate which would normally be lost or unused, and much research is currently in progress in the United States on the extraction of uranium and the production of alumina and phosphate fertilizer from the aluminum phosphate zone.

## REFERENCES CITED

Altschuler, Z. S., Cisney, E. A., and Barlow, I. H., 1953, X-ray evidence of the nature of the carbonate-apatite [abs.], *in* Saint Guilhem, P. L. R., ed., Origine des gisements des phosphates, des chaux: Internat. Geol. Cong., 19th Algiers, Comptes rendus, sec. 11, fasc. 11, p. 9.

Altschuler, Z. S., Clarke, R. S., and Young, E. J., 1954, Uranium in apatite [abs.]: Geol. Soc. America Bull., v. 65, p. 1539.

Arambourg, Camille, and Orcel, Jean, 1951, Observations preliminaires sur la présence d'un vanadate d'urane dans les gisements de phosphates du Maroc: Acad. sci. Paris Comptes rendus, v. 233, p. 1635–1636.

Baes, C. F., Jr., 1954, The production of U $^{4+}$ by ferrous ion in phosphoric acid solution; the formal electrode potential of the U $^{4+}$—U $^{6+}$ couple: U. S. Atomic Energy Comm. ORNL–1581 or AECD–3594 (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries).

Capdecomme, Laurent, 1953, Etude minéralogique des gites de phosphates alumineux de la region de Thiès (Sénégal), *in* Saint Guilhem, P. L. R., ed., Origine des gisements des phosphates des chaux: Internat. Geol. Cong., 19th, Algiers, Comptes rendus, sec. 11, fasc. 11, p. 103–117.

Capdecomme, Laurent, and Pulou, Réne, 1954, Sur la radio-activite des phosphates de la region de Thiès (Sénégal): Acad. sci. Paris Comptes rendus, v. 239, p. 288–290.

Cathcart, J. B., 1950, Notes on the land-pebble phosphate deposit of Florida, *in* Snyder, F. G., ed., Symposium on mineral resources of the Southeastern United States: Knoxville, Tenn. Univ. Press, p. 131–151.

Cathcart, J. B., Blade, L. V., Davidson, D. F., and Ketner, K. B., 1953, The geology of the Florida land-pebble phosphate deposits, *in* Saint Guilhem, P. L. R., ed., Origine des gisements des phosphates des chaux: Internat. Geol. Cong., 19th, Algiers, Comptes rendus, sec. 11, fasc. 11, p. 77–91.

DuToit, A. L., 1917, The phosphates of Suldanha Bay: South African Geol. Survey Mem. 10, 34 p.

Garrels, R. M., 1955, Some thermodynamic relations among the uranium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: Am. Mineralogist, v. 40, p. 1004–1021.

Goldschmidt, V. M., (edited by Alex Muri), 1954, Geochemistry: Oxford, Clarendon Press, 730 p.

Guntz, A. A., 1952, Sur la présence d'uranium dans les phosphates Nord-Africains: Acad. sci. Paris Comptes rendus, v. 234, p. 868–870.

Jacob, K. D., Hill, W. L., Marshall, H. L., and Reynolds, D. S., 1933, The composition and distribution of phsophate rock with special reference to the U. S.: U. S. Dept. Agr. Tech. Bull. 364, 90 p.

McKelvey, V. E., Cathcart, J. B., Altschuler, Z. S., Swanson, R. W., and Buck, K. L., 1953, Domestic phosphate deposits, *in* Pierre, W. H., and Norman, A. G., eds., Soil and fertilizer phosphorus in crop nutrition, Volume IV of Agronomy: New York, Am. Soc. Agronomy—Academic Press, Inc., p. 347–376.

McKelvey, V. E., and Nelson, J. M., 1950, Characteristics of marine uranium-bearing sedimentary rocks: Econ. Geology, v. 45, p. 35–53.

MacNeil, F. S., 1947, Correlation chart for the outcropping Tertiary formations of the eastern gulf region: U. S. Geol. Survey Oil and Gas Inv. Prel. Chart 29 (with text).

Moore, G. W., 1954, Extraction of uranium from aqueous solution by coal and other materials: Econ. Geology, v. 49, p. 652–658.

Neuman, W. F., Neuman, M. W., Main, F. R., and Mulryan, B. J., 1949, The deposition of uranium in bone, V—Ion exchange studies: Jour. Biol. Chemistry, v. 179, p. 335–340.

Palache, Charles, Berman, Harry, and Frondel, Clifford, 1951, Dana's system of mineralogy, v. 2, 7th ed.: New York, John Wiley and Sons, Inc., 1224 p.

Russ, W., 1924, The phosphate deposits of Abeokuta province: Nigeria Geol. Survey Bull. 7, p. 9–38.