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SUMMARY OF WORK ON THE MINERALOGY AND PETROGRAPHY OF
SOUTHEAST PHOSPHATES THROUGH APRIL 1952*

By

Z. S. Altschuler

November 1952

Trace Elements Investigations Report 266

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SUMMARY OF WORK ON THE MINERALOGY AND PETROGRAPHY
OF SOUTHEAST PHOSPHATES THROUGH APRIL 1952

By

Z. S. Altschuler

ABSTRACT

The phosphate deposits of the Florida land-pebble field occur in the Bone Valley formation of Pliocene age. The Bone Valley formation is underlain by marine phosphatic dolomite and limestone of Miocene age and overlain by surface sands of probable Pleistocene age. Approximately the lower three-fourths of the Bone Valley formation is mined. This part is called matrix. The upper quarter of the formation together with the overlying loose quartz sands is discarded as overburden.

The matrix of the Bone Valley formation is a pebbly, clayey, phosphatic sand, characterized by crude graded bedding. It consists essentially of quartz, montmorillonite, and apatite. The latter, almost entirely clastic, contains substantially all of the uranium in the matrix.

The upper part of the Bone Valley formation is normally a massive-bedded, clayey, quartz sand of low uranium content. However, it is the locus of a zone of leaching, mineralogic alteration, and enrichment in uranium. In unaltered state its intergranular cement consists of either kaolinite or fine-grained nonclastic apatite. In the leached zone the predominant minerals are pseudowavellite and wavellite. In addition,

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kaolinite, phosphosiderite, and gibbsite may be present in minor or trace quantities in the leached zone.

In contrast to matrix rock which contains from 10 to 20 percent P_2O_5 and approximately 0.008 percent uranium, leached-zone rock typically has 8 to 12 percent P_2O_5 and approximately 0.012 percent uranium.

It is possible to speak of the upper and the lower parts of the Bone Valley formation by virtue of a marker horizon separating the two zones. This horizon is placed at the transition between a zone of pebbly graded beds and the overlying massive-bedded clayey sand. The sequence represented by these two types has been found in both leached and unleached rock.

In this report the mineralogy and uranium contents of Southeast phosphates are discussed with reference to the lithologic units of the Hawthorn and Bone Valley formations and to waste slimes. In addition, the immediate problem of sampling leached-zone rock for process development studies is discussed and plans for future work (fiscal 1953) are presented.

INTRODUCTION

Trace Elements Section Washington Laboratory work on phosphate rock on behalf of the Atomic Energy Commission has been in progress since the fall of 1948. It was not until January 1949, however, that personnel were assigned permanently and exclusively to phosphate study. Prior to this, samples collected by J. C. Rabbitt from pits and plant processing

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were studied by various members of the laboratory for short periods of time. These more or less exploratory studies revealed two important facts regarding the normal matrix rock: (Thompson et al., 1949).

1. The major mineral phase -- the host for practically all of the uranium -- is a member of the apatite group; no uranium minerals or other important secondary carriers of uranium were found.

2. Although the phosphate showed great variety in appearance and physical properties, the uranium within the rock could not be significantly concentrated by separations based on any of these properties (magnetism, hardness, color, luster, specific gravity, and size) except fluorescence.

In January 1949, Z. S. Altschuler and C. E. Boudreau were assigned to study of the Southeast phosphates. Field work was undertaken from January 20 to March 25, 1949. In the company of Botinelly, Ingerson, Rabbitt, and Rove we were introduced to the phosphate field by J. B. Cathcart. The impression gained among all of us was that we were faced with a deposit on which there was no available information as to zonal or areal differences in uranium content.

Field work by laboratory personnel during this period was devoted to collecting samples and geologic information. Forty-two stratigraphic sections were measured and studied in detail and 700 samples were taken for the purpose of outlining the occurrence and distribution of the various types of phosphate deposits within the "land pebble" field and determining their uranium contents.

After the construction of detailed graphic logs for the sections measured it was seen that no readily perceptible stratigraphic markers exist in

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the Bone Valley formation; local correlations can be made, however, between facies, zones, and groups of features. The top of the Bone Valley formation is marked by color changes and by the abrupt change in lithology to the overlying Pleistocene quartz sand. The boundary between the Bone Valley and the underlying Hawthorn formation varies both in its expression and its stratigraphic position, but it too could be recognized lithologically and by a group of associated features, including evidence of solution and reworking of the limestone, local residual hardpans of siliceous or hematitic material, local residual clays, and, commonly, an abrupt change to the more distinctly bedded and more clastic phosphate deposit.

The uranium distribution within the phosphate beds was studied with two aims; first, to find and delimit any uranium-rich zones more amenable to commercial exploitation; second, to determine the actual nature of the uranium occurrence. To attain these ends, field studies were made of the fluorescence of the rock in place by using a Mineralight on night trips, and then lithologic zones and areas of high fluorescence were checked by Geiger counter. A general correspondence in the results was noted. In addition, semiquantitative fluorimetric tests for uranium were made in the field on samples from different zones throughout the commercial phosphate field. Laboratory study just prior to the initiation of field work 1/

1/ A laboratory study of pebbles from a conglomeratic sample of phosphate rock revealed "...a striking increase in uranium content from the surface (of the pebbles) inward..." It was then stated that this gradient "... suggests leaching of the uranium from phosphate pebbles of originally more uniform richness..." (Altschuler, 1949a)

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indicated that leaching may be a very important factor governing the uranium distribution within the phosphate rock. The testing program described above showed that the richest uranium-bearing phosphates in the Florida field occur in a leached zone in the upper part of the Bone Valley formation and that this zone, although variable in thickness and locally absent, is a moderately extensive feature. (This was reported in the monthly report for March 1949.)

The existence of rich leached rock had already been noted by the resident field party (Staff, 1949). However, upon these further proofs of its extent and of its consistently richer nature, a program of laboratory study of this zone was started in place of the previously proposed laboratory survey of all of the Bone Valley. This work included chemical, mineralogic, and mechanical analyses. It was devoted to finding out

- 1) which minerals were present,
- 2) their uranium contents,
- 3) why the leached zone is rich in uranium, and
- 4) the nature of the uranium occurrence.

In essence, all work of the laboratory since January 1949 has been addressed to the above four problems. Unfortunately each of these problems is many-sided. Thus, desire to comprehend completely the leached zone made necessary the assumption of stratigraphic studies. The desire to understand the mineralogy and nature of uranium occurrence led to detailed studies of the carbonate-apatite problems. The desire to

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synthesize uraniferous apatite led to an extensive survey of the literature on apatite synthesis.

In many other types of deposits collateral problems do not arise to the same extent. Unfortunately, all Survey work on the land-pebble field has entailed excessive expenditure of time due to the lack of geologic control and to the petrographic nature of phosphate ores which limits the application of optical microscopy and makes difficult normal laboratory-separation techniques.

As this report is mainly a digest and summary of other reports, it is difficult to acknowledge our specific debts to those of our colleagues who have furnished data and help throughout the course of our investigations. This help, however, has been large and continuous over the past three years, and we feel that special mention should be made of the guidance and assistance of J. C. Rabbitt and T. Botinelly, the chemical work of F. S. Grimaldi and his staff, the X-ray work of E. Cisney, the spectrographic work of C. L. Waring and his staff, and the editorial assistance of Jane Titcomb. Recent work on the leached zone has been carried out with the help of J. P. Owens and R. Berman. In addition we have been greatly aided by the cooperation of the Survey's field party under J. B. Cathcart.

In the following pages the emphasis is placed on mineralogy; discussion of genesis and of descriptive petrography has been limited merely to what is necessary to establish the setting of the mineral occurrences.

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BRIEF STRATIGRAPHIC DESCRIPTION OF THE
FLORIDA LAND-PEBBLE FIELD

The phosphate deposits of the Florida land-pebble field are those of the Bone Valley formation. The Bone Valley overlies the Miocene Hawthorn formation, and is overlain by a deposit of loose quartz sands of probable Pleistocene age.

The Bone Valley formation is approximately 35 feet thick, although its thickness may vary considerably. It is made up of pebbly and clayey sands characterized by crude graded bedding. Approximately the upper quarter of the formation, however, is clayey sand characterized by massive bedding. This upper zone, together with the overlying quartz sand is treated as "overburden". The lower three-fourths of the Bone Valley formation constitutes the zone mined commercially and known as "matrix".

At the top of Bone Valley is a zone, ranging from several inches to 13 feet in thickness, known as the leached zone. It is fairly widespread but may be locally absent. It is characterized by its gray to white color, vesicularity, and the low specific gravity of its rock, all of which result from leaching and alteration by ground water. This zone may be confined to the upper massive-bedded part of the Bone Valley formation or it may extend into the "matrix" zone. The mineralogy, textures, and uranium contents of the leached zone in a particular locality depend greatly on whether the upper or both of the original lithologic zones of the Bone Valley formation have been leached.

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In some areas the Bone Valley is immediately underlain by a few feet of soft clay rather than hard calcareous rock. This type of deposit is known as "bed clay" in the land-pebble field.

In describing the minerals of the Southeast phosphates we can conveniently consider them in terms of six lithologic and genetic zones, as listed below:

Pleistocene (?) quartz sands
Upper Bone Valley formation - unleached
Upper Bone Valley formation - leached zone
Bone Valley formation - matrix
Hawthorn formation - bed clay
Hawthorn formation - bedrock

MINERALOGY

The Hawthorn formation

Bedrock zone

The Hawthorn formation is known as "bedrock" in the land-pebble district, and it underlies all of the Bone Valley formation. In mining very little of the Hawthorn formation is exposed along mining faces, and if exposed it is usually not penetrated beyond a depth of 5 feet. Thus, information on the Hawthorn formation is restricted to samples from its upper few feet in mine exposures and to well cuttings from deep drilling. Mine samples of the Hawthorn have been studied from the following local-

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ities in the phosphate field: Sidney, Noralyn, Pauway, Peace Valley, Alafia River exposures, and Plant City.

In each of these areas the rock available (bedrock, subjacent to matrix or bed-clay) was siliceous and phosphatic dolomite. The dolomite is fine-grained and some of it is leached; it contains residual concentrations, in pockets and seams, of quartz, nodular apatite, and clay.

During the course of field work in 1951, three wells in the Hawthorn formation were logged by binocular microscope at the offices of the Florida Geological Survey to obtain a rough estimate of the apatite content of deeper Hawthorn rock. The following table summarizes this information:

<u>Well location and Florida Geological Survey no.</u>	<u>Thickness of sand cover (feet)</u>	<u>Thickness of Hawthorn (feet)</u>	<u>Range in percent of nodular apatite content</u>
Sarasota, W-2318	5	80	1 - 10
Laurel, W-1897	20	305	1 - 8
Venice, W-837	10 (qtz. sand plus shell frag.) 24 (qtz. sand, 1 percent apatite nodules)	80	1 - 5

During 1952 Robert Berman has been conducting a detailed mineralogic study of well cuttings from a deep well at Cone's Dairy, Plant City, Fla. His results, tabulated below, reveal the changes in lithology in the Bone

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Valley and Hawthorn formations.

<u>Depth in feet</u>	<u>Clay type and percent</u>	<u>Carbonate type and percent</u>	<u>Apatite percent</u>	<u>Quartz percent</u>
10	Montmorillonite* and organic matter, 10	Dolomitized shell, 10	2	78
20	Montmorillonite, 36		2	62
30	Montmorillonite, 85		5	10
40	Montmorillonite-major) attapulgitic-minor) 55	Dolomite, 5	20	20
48	Attapulgitic,** 15	Dolomite, 40	15	30
55	Attapulgitic, 50	Dolomite, 5	15	30
60	Attapulgitic, 5	Dolomite, 83	2	10
70		Dolomite, 94	1	5
74		Dolomite, 83	5	12
78		Dolomite, 45	20	35
80		Calcite (major) and Dolomite (minor) 97	1	2
90		Calcite, 54	1	45
100		Calcite, 40	3	47
110		Calcite, 57	3	40

*Montmorillonite $(Al, Mg, Fe)_4(OH)_4(Si, Al)_8O_{20} \cdot 8H_2O$
 **Attapulgitic $Mg_5Si_8O_{20}(OH)_2 \cdot 10H_2O$

On the basis of our knowledge of other sections the contact of the Bone Valley with bed clay would occur in the vicinity of the 48 foot sample, or at the first prominent occurrence of attapulgitic. Similarly, the

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"bedrock" would also begin close to this horizon as this is the first prominent occurrence of dolomite. The change to calcite at 80 feet is significant. It cannot be told from the drill samples, however, whether the upper dolomitic zone is a replacement or an original stratigraphic unit.

Bed clay zone

Bed clay is the term used in the land-pebble district for the discontinuous deposits of soft, water-saturated, and highly plastic clay that occur beneath the matrix. These clay deposits are seldom more than 2 feet thick and occur in continuity with the Hawthorn formation, from which they can be seen to grade in color, hardness, and water content. In recognition of the above-mentioned grading and the fact that the bed clay is usually overlain by bedded, clastic material, the bed clay is here assumed to derive by post-depositional alteration from the underlying Hawthorn formation. The bed clay has been identified in a number of localities: Noralyn, Peace Valley, Homeland, Saddle Creek and Plant City and from prospect drilling south of Ft. Meade and north of Lakeland. In every one of these localities attapulgite was a prominent constituent, and in most of them montmorillonite also occurred in slightly lesser quantity. Attapulgite was first identified in the Bone Valley formation by E. J. Dwornik in the course of electron microscope studies of randomly selected slimes. The identifications in the bottom clays were based on X-ray spectrographic studies and confirmed

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by electron microscope examination.

At present, it is as difficult (and less important) to cite an average mineral composition for bed clay as it is for any other zone in the district. Based on the relative intensities of peaks in X-ray spectrographs and the relative prominence of the two phases seen in electron microscope study, it can be stated that the clay fraction of the bed clay is approximately 60 percent attapulgite and 40 percent montmorillonite.

In addition to clay, the insoluble portion of the Hawthorn formation is also concentrated in the bed clay. Thus chert, quartz, apatite, and accessory minerals are found in varying amounts and proportions, depending on the amount of earlier erosion and later leaching sustained by the Hawthorn formation.

The Bone Valley formation

Matrix zone

The matrix is that portion of the Bone Valley formation which is mined.^{2/} Together with the overlying clayey sands it makes up the total Bone Valley formation. It is characterized by pebbly and clayey textures and crude graded bedding. In the individual graded sets, the coarser clastic units are made up of apatite sand and pebble which give way up-section to clayey quartz and phosphate sands or quartzose clays. Although

^{2/} Occasionally bed clay is sufficiently enriched in phosphate to be mined as ore. In such instances bed clay would also be called matrix.

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locally the lithology and thickness vary greatly, the sequence of pebbly phosphorite grading upward to sandy clay is basic throughout the land-pebble area.

The composition of single beds of the matrix ranges from almost pure clays to almost pure apatite conglomerates or sands. The average, however, of the deposit is approximately as follows:

Apatite (carbonate-fluorapatite)	35 percent
Clay ^{3/} (montmorillonite)	35 percent
Quartz and minor chert	30 percent

The accessory mineral content of the matrix is similar to that of the Upper Bone Valley formation, which is described several pages below.

Nature of the apatite

The fine-grained isotropic apatite of the Bone Valley formation, in contrast to igneous apatite, is characterized by .

- a) A deficiency in P_2O_5 content of from 2 to 4 percent
- b) An excess of F_2 content of approximately 0.5 percent
- c) The presence of approximately 3 percent of carbonate.

Most marine apatite is of similar nature and also contains more uranium than "crystalline" apatite. For this reason it has been extremely important to determine the mineralogic nature of carbonate-fluorapatite. Thus, if carbonate-bearing fluorapatite is not significantly different from

^{3/} The matrix clay has not been studied in every locality within the district. However, it has been identified as montmorillonite in every vicinity from which it has been determined. These are Varn, Pauway, Achan, Bonny Lake, Noralyn, and Plant City.

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normal fluorapatite, it is possible that its uranium might be solely or in large part a function of the carbonate or excess fluorine and might be present as separate mineral phases -- uranous or uranyl fluorides or carbonates.

Carbonate-apatite has engaged the attention of physiologists, mineralogists, and chemists for over half a century. Regarding it two points of view prevail: one maintains that carbonate occupies a structural site, the other states that carbonate-apatite is merely apatite with an included carbonate phase. The proponents of the latter view maintain that it is impossible to distinguish carbonate-apatite from carbonate-free apatite by X-ray. On this basis they justify the inferences made from leaching experiments and heating curves that bone, teeth, phosphorite, and well-crystallized vein occurrences of carbonate-apatite are all similar mixtures of carbonate and apatite.

The essential point of departure is the interpretation of the X-ray data. Despite the fact that many investigators have for many years claimed that differences exist, each year witnesses the publication of additional papers claiming the differences to be nonexistent, unimportant, or due to the stray emplacement of the minor or trace elements common in apatite.

It has obviously become necessary to resolve this impasse by conducting experiments designed to test the significance of the differences in X-ray patterns. This was done in the following experiments:

1. Several samples each of pure analyzed material, representing end-members of fluorapatite and hydroxylapatite and samples of carbonate-fluor-

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apatite containing 2 to 4 percent CO₂ were X-rayed by powder-film methods under identical conditions of instrumentation and sample preparation. The resultant film patterns were distinctive and could be correlated, by sight, with the above chemical types.

2. Mixtures of these chemical varieties of apatite were X-rayed with the result that line duplication or line broadening obtained.

3. Mixtures of two specimens of the same type of apatite were X-rayed with the result that neither line broadening nor duplication occurred and the film patterns could not be distinguished from those of individual samples.

4. X-ray spectrometer patterns were obtained of an accuracy and precision equivalent to 0.001 A. The results, tabulated below, offer definite proof that carbonate-fluorapatite differs from hydroxyl or fluorapatite.

Comparison of unit-cell constants in A units

	a _o	c _o	c/a
Hydroxylapatite, Holly Springs, Georgia	9.413	6.875	0.730
Fluorapatite, Durango, Mexico	9.386	6.878	0.733
Carbonate-fluorapatite, Stafell, Germany	9.344	6.881	0.736

In addition to the above X-ray work, carbonate-apatite has been studied chemically by the use of staining agents and preferential solvents (Silverman, Fuyat, and Weiser, 1951). It has been found that in phosphorite, in contrast to well-crystallized carbonate-fluorapatite, some of the carbonate is present as finely dispersed calcite that could be leached without lowering the uranium content of the rock. Analysis after leaching reveals the

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presence of more carbonate, although material before and after leaching gives the same carbonate-fluorapatite X-ray pattern. Thus, although phosphorite may contain discrete carbonate phases, the apatite in phosphorite also contains carbonate in its structure.

It has been found that the apatite in most marine phosphorite is carbonate-fluorapatite. This is true of nodules or pellets in the Hawthorn formation and the Phosphoria formation, and in the deposits of French Morocco.

The upper part of the Bone Valley formation

The Bone Valley formation may be separated by an unconformity from the overlying quartz sands. The unconformity is marked by a sharp lithologic break and the development of hardpan. Regardless of whether the unconformity is an original feature or a secondary one caused by leaching and hence only an apparent unconformity, it marks the limit of the Bone Valley formation lithologically.

Unleached rock

The upper Bone Valley in unweathered state is a clayey quartz sand. The cement may be kaolinite, or clay-sized apatite with continuous clay-like textures. Montmorillonite is absent in most localities. This interstitial cement comprises about 30 percent of the rock, the remainder being made up almost entirely of quartz. The zone contains from 1 to 1 1/2 percent of heavy minerals and, locally, minor (< 5 percent) amounts of

limonite and hematite. This fresh clayey sand is called Bartow clay by some of the miners.

The leached zone

The leached zone is that portion of the Bone Valley formation which has been postdepositionally leached and altered. It cannot be thought of as a stratigraphic unit. Its boundaries are irregular and discordant to the bedding. As leaching has progressed from the top downward, the leached zone is confined to the upper part of the Bone Valley formation; locally, however, the basal portion of the leached zone extends into what had previously been matrix (that is, originally pebbly and apatitic).

The physical and mineralogic properties of the leached zone depend greatly on the original texture and composition of the rock. A tabulated comparison of some of these properties follows.

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<u>Property</u>	<u>Unleached rock</u>	<u>Leached rock</u>
Color	Light green or gray	White or cream, orange- and brown-stained
Specific gravity	Approx. 2.5	2.5 to less than 1.0
Coherence	Compact and plastic when wet; indurated when dry	Generally friable
Effective porosity	Generally less than 10 percent	40 - 60 percent
Texture	Homogeneous clayey sand in upper unit; graded, pebbly sand in lower unit	Visibly porous; coarse matrix textures preserved at base, even to the extent of graded porosity in previously graded bedding.
Composition	Quartz, about 70 percent Cement, mainly kaolinite, with lesser apatite and montmorillonite	Quartz, about 75 - 80 percent Cement, Wavellite, $Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$ Pseudowavellite, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$ Phosphosiderite, $(Fe,Al)PO_4 \cdot 2H_2O$ Kaolinite, $Al_4(OH)_8Si_4O_{10}$ Apatite, $Ca_9(PO_4)_6CaF_2$ Gibbsite, $Al_2O_3 \cdot 3H_2O$ Diaspore, $Al_2O_3 \cdot H_2O$ Manganese oxide

The accessory mineral suite, common to both leached and unleached rock, is listed below. The total suite makes up about 1 1/2 percent of the rock, distributed among the constituents in roughly the proportions listed. The minerals are listed in order of probable importance. No attempt is made to

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tabulate a completely quantitative average. This problem will be discussed below.

Hematite and goethite	30.0
Ilmenite and leucoxene	25.0
Zircon	23.0
Staurolite	3.0
Sphene	3.0
Rutile	2.0
Garnet	1.5
Magnetite	<1.0
Tourmaline	<1.0
Monazite	<1.0
Epidote	<1.0
Kyanite	<1.0
Igneous apatite	<1.0

The above accessory mineral assemblage will naturally vary according to location and degree of leaching. Thus, alteration products (such as hematite, goethite, and leucoxene) will be less prominent in unleached rock; manganese oxides (exact type still undetermined) are locally very prominent in leached rock; and magnetite, which is common in matrix rock and unleached upper Bone Valley, "weathers out" of leached rock.

The principal phosphate minerals in the leached zone are pseudowavellite, wavellite, and apatite. One other phosphate mineral appears as a major

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constituent of some leached-zone rock. It has recently (October 1952) been proved to be millisite $[(Na,K)CaAl_6(PO_4)_4(OH)_9 \cdot 3H_2O]$ by J. P. Owens on the basis of its X-ray identity with millisite from Fairfield, Utah (Larsen, 1942). It is believed that millisite accounts for the reported occurrences of phosphosiderite, which we have been unable to find. It should be noted that phosphosiderite has been cited as a major constituent in some occurrences of the leached zone by Hill, Armingier, and Gooch (1950); however, detailed identifications have not been presented. Gibbsite also has been found to be a minor constituent of leached-zone rock on the basis of X-ray study. This identification also rests on the presence of extra lines in X-ray patterns and is not conclusive as attempts to separate the gibbsite have proved futile.

In summarizing, it can be stated that the leached zone is a secondarily altered and uranium-enriched portion of the Bone Valley formation. Its uranium was concentrated by the action of ground water probably through the combined processes of residual and downward enrichment. The uranium within the leached zone is most strongly associated with the calcium phosphate (apatite) and to a lesser extent with the calcium aluminum phosphate (pseudowavellite) and the aluminum phosphate (wavellite). Although one uranium mineral, autunite, was found in the leached zone, it is known to occur in only one place and the bulk of the Bone Valley's uranium is, as far as presently determined, tied up with phosphate minerals; quartz

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makes up a great part of the leached zone. Clay is a minor constituent and carries very little uranium. No correlation has been found between uranium content and color, size, specific gravity, magnetism or any other inherent property of the phosphate minerals, except insofar as any of these can be associated with composition, leaching, or secondary precipitation.

Overburden sands

The topmost zone over most of the field consists of loose quartz sand. The rare and local instances where cements are present are either in soils or small lake beds. There the cements consist of kaolinite clay and limonite or goethite. These soils may be humus-stained. No uranium and no phosphate, other than in traces, is present in this zone except in the basal portion as inclusions or relicts of the underlying Bone Valley. The quartz is moderately well rounded, very well sorted, and depending on locality, medium- to fine-grained.

Uranium contents of minerals in the land-pebble field

Due to differences in geologic history, individual minerals present in the land-pebble field will show considerable variation in their uranium content. For this reason, uranium contents are listed as follows in terms of typical content and range rather than in averages.

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<u>Mineral</u>	<u>Mode</u>	<u>U content (percent range)</u>
Apatite		
Nodules in Hawthorn	0.005	0.003 - 0.008
Pebbles in matrix	0.008	0.003 - 0.050
Pebbles in basal leached zone	0.020	0.010 - 0.100
Wavellite	0.012	0.005 - 0.050
Pseudowavellite	not tested in pure state	
Montmorillonite	0.001	< 0.002 *
Kaolinite	0.001	< 0.002 *
Calcite	0.001	< 0.002 *
Dolomite	0.001	< 0.002 *

*Little information is available on the range in uranium content of these minerals, which have not been as extensively tested as the others. It is believed that 0.002 percent is a good upper limit.

Mineralogy of washer-plant waste slimes

In December 1949 an investigation was made of the mineralogy and uranium content of samples of phosphate waste slimes. Slime materials are mineralogically like the Bone Valley formation as a whole. However, the slimes show the greatest possible variation in compositional proportions. This is due to the manner of deposition of slimes. They are pumped out of effluents into abandoned mines and immediately undergo sorting with the results that in a single slime deposit one may find pure quartz, pure apatite, pure clay, and mixtures of some and all of these. There has been

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insufficient explicit recognition of this, and it is the writer's hope that this digression will be excused because the heterogeneity of the slimes affects profoundly such considerations as

- 1) Average composition, average U or P₂O₅ contents;
- 2) Recovery of P₂O₅ or U from slimes;
- 3) Sampling of slimes for process studies (as for light-weight aggregates, bloating characteristics, recovery characteristics, etc.).

The "slimes" can be thought of in terms of two general types (which are not entirely mutually exclusive):

1. Simple fine-grained mixtures (of single grains) containing apatite, quartz, minor amounts of calcite and feldspar, and the accessory minerals.

2. Complex fine-grained mixtures (of aggregate grains) containing clay-phosphate aggregates, phosphate aggregates, pure clay, pure apatite, minor amounts of calcite and feldspar, and the accessory minerals.

The essential distinction between the two groups is the presence of much alumina. In the second category the pure mineral grains are not major constituents and the aggregate grains persist in the finest material examined (-400 mesh). The second clay-rich type is much more common.

The clay-phosphate aggregates referred to above are composed of montmorillonite, apatite, pseudowavellite, wavellite, and quartz. Much of this material may have been formed by flocculation during hydroseparation treatment in the phosphate plants. The phosphate aggregates, in contrast, are inherited and are composed of apatite replaced in varying degree by

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pseudowavellite and/or wavellite.

The following table gives representative analyses of slimes.

Sample number	U percent	P ₂ O ₅ percent	Composition percent	
Lot 863 no. 2	0.009	11.0	Montmorillonite	55
			Apatite	20
			Pseudowavellite and wavellite	10
			Quartz	10
			Others	5
Lot 828 no. 75	0.012	23.0	Apatite	55
			Quartz and accessories	40
			Calcite	3
			Wavellite	2
Lot 828 no. 8	0.002		Quartz and accessories	97
			Apatite	3

Magnetic and heavy-liquid separations were made on sized fractions of "slimes" in efforts to concentrate the uraniferous material. In samples of type 1 this can be done merely by removing quartz. Material of the clay-rich type cannot be easily beneficiated, however, as most of the particles are aggregates, even in the finest size. The most effective separations were obtained by screening and heavy liquids and it was generally found that concentration of apatite corresponded to concentration of uranium as can be seen from the following illustrations.

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Sample number	Fraction	Composition percent	U percent	
Lot 828 no. 1	150-200 mesh light	Montmorillonite	60	0.024
		Apatite	20	
		Pseudowavellite and wavellite	20	
	150-200 mesh heavy	Apatite	85	0.033
		Calcite	8	
		Pseudowavellite and wavellite	7	
Lot 821-8	270-325 mesh light	Montmorillonite	35	0.020
		Pseudowavellite and wavellite	35	
		Apatite	30	
	270-325 mesh heavy	Apatite	60	0.024
		Pseudowavellite and wavellite	20	
		Montmorillonite Quartz	10 10	

The above section on slimes is abstracted from the original report on this work issued on January 11, 1950 (Altschuler, 1949b).

The minerals found to occur in the zones of the land-pebble field are tabulated in figure 1.

Various additional projects have been undertaken in conjunction with the Southeast phosphate studies. These are not treated in this report owing to their lack of immediate pertinence or to the fact that information obtained was not in all cases new or different from what is published in the

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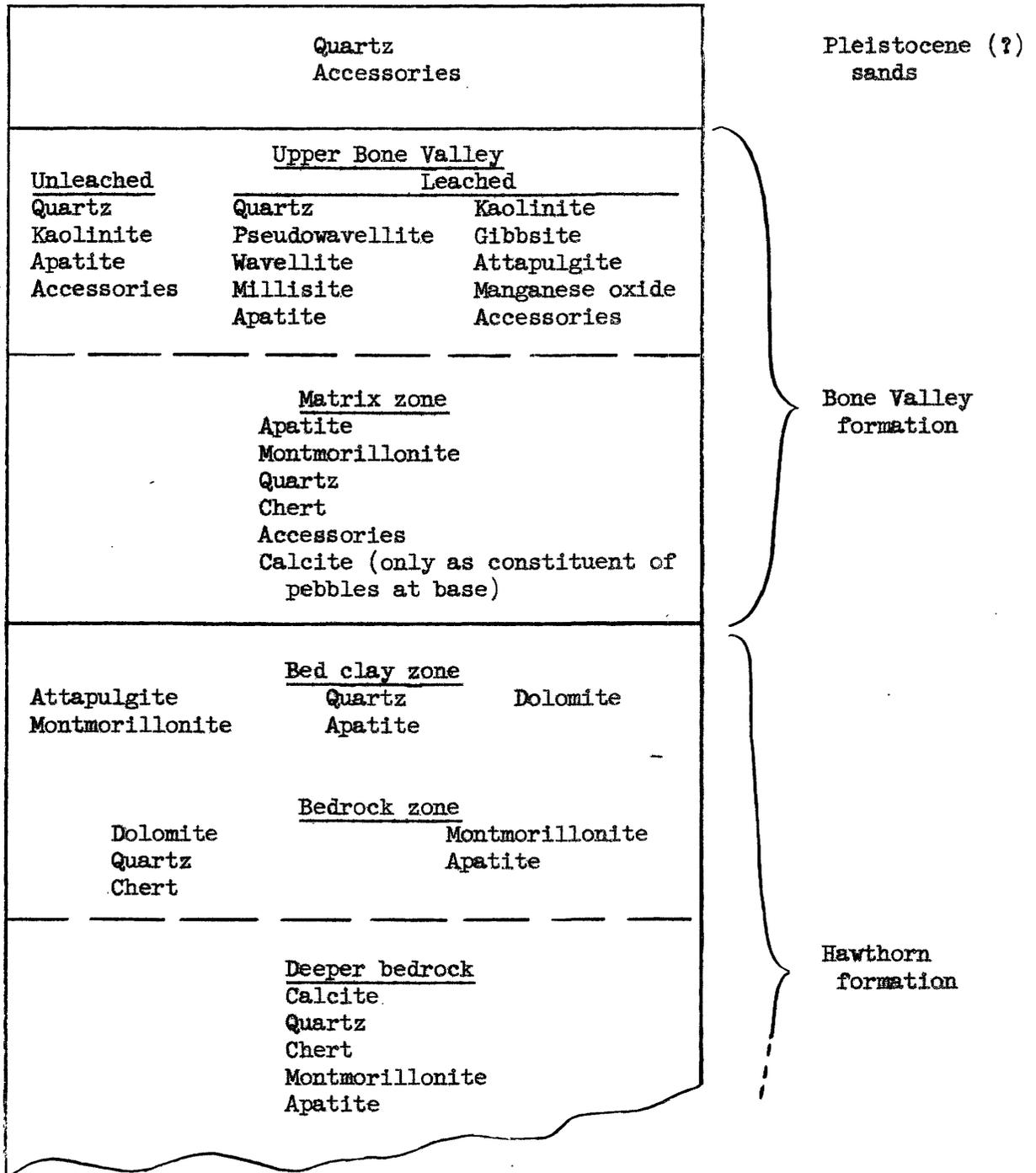


Figure 1.--Mineral occurrences in the land-pebble field

literature. Some of these projects are listed below.

1. Spectrochemical study of trace elements in apatite.
2. Uranium content of nonmarine apatite.
3. Mineralogy and chemical composition of Mona Island phosphates.
4. Mineralogy and uranium distribution of Moroccan phosphates.
5. Survey of the literature on apatite synthesis.
6. Synthesis of apatite.

THE STRATIGRAPHY OF THE UPPER PART OF THE BONE VALLEY FORMATION
AND THE RELATION OF THE LEACHED ZONE TO STRATIGRAPHY

In early studies of the chemistry and mineralogy of the leached zone (Altschuler and Boudreau, 1949) the descriptive petrology of leached rock was documented and it was demonstrated that residual and downward secondary enrichment of uranium have occurred. However, in order to understand satisfactorily the origin of the leached zone it is necessary to compare stratigraphically equivalent leached and unleached materials of identical or comparable original lithologies. Unfortunately, no stratigraphic control had been established in the land-pebble field in 1950. Thus it was necessary to search for particular cases of beds or zones extending from leached into unleached material. Such cases could exist by virtue of either of the following conditions:

1. A locally irregular leached zone.
2. Post depositional dip or slump preceding the advent of leaching.

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During field work in February 1950 in the Homeland area, both of these conditions were found auspiciously combined with well-developed stratification, which permitted the tracing of an individual pebble band over the full length of the mine.

It was thus possible to study, sample, and map in detail both the original and the postdepositional changes in the upper Bone Valley. The essential findings of this study are summarized in the following paragraphs, which are paraphrased from a report by Altschuler, Jaffe, and Dwornik (1951).

The two topmost zones of the Bone Valley formation at Homeland are:

1. A clay- or phosphate-cemented quartz sandstone characterized by massive bedding.
2. An underlying pebbly or conglomeratic quartz and phosphate sand characterized by graded bedding (this is equivalent to the top of the matrix). This sequence is found in every other area of the land-pebble field, and in fresh as well as in leached rock. Therefore the zones described are considered to be primary stratigraphic features and the transition between them to be a valid key horizon.

The change between the two zones is gradational although it occurs within a vertical distance of only a few inches. The topmost layer in the zone of graded beds is a conglomeratic sand or sandy conglomerate. The basal few inches of the clayey quartz sand may contain 5 to 10 percent of phosphate granules; however, clastic phosphate is absent from the remainder of the clayey quartz sand. In addition, the small amount of clastic phosphate in

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the basal clayey sands is smaller in size than that in the underlying graded beds.

Thus, the important features of the marker horizon are:

1. The vertical change, within a few inches, from graded to massive bedding.
2. The lack of clastic phosphate in all but the basal part of the clayey quartz sand.
3. The decrease in size of the clastic phosphate in the basal part of the clayey sand zone.

These zones represent the most important original geologic controls in the development of the leached zone. They affected the subsequent textures, the subsequent uranium concentrations, and, to an extent not yet completely known, the subsequent mineralogy.

The leached zone encompasses either the upper or both of the zones. As a result, rock from the leached zone may have two different aspects. The upper unit, after leaching, is not obviously porous and in places has the appearance of a pure quartz sand. The lower unit, when leached, develops large cavities. The upper unit, when leached and altered, may have pure wavellite in addition to quartz. The lower unit after leaching and alteration, always contains some mixture of wavellite, pseudowavellite, variscite-strengite (?) and quartz. The softened and porous apatite pebbles at the base of the leached part of the lower unit act as natural filters for descending uranium-bearing ground waters and become the sites of greatest enrichment in the land-pebble field.

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In addition to its bearing on the understanding of the leached zone the establishment of stratigraphic control in the Bone Valley formation greatly enlarges the opportunity for further geologic work in the land-
pebble field. It is a key to such studies as relation of leaching to depth, topography, lithology, and deformation, as well as to the possible further stratigraphic subdivision of the Bone Valley formation.

THE PROBLEMS OF THE LEACHED ZONE AND IMMEDIATE FUTURE PLANS

Two problems of immediate economic importance which demand mineralogic and petrographic work are:

1. Regional variations in the mineralogic composition of the leached zone.
2. The mode of occurrence of uranium in leached-zone rock.

The first problem, that of the average or regional mineralogic composition of the leached zone, requires extensive sampling for its solution. It is known that pseudowavellite predominates in some localities and wavellite in others. Are the differences regional, areal, or local and sporadic? This affects sampling for process control and predictions of uranium production.

The second problem can be framed thus: is the leached zone or some fraction of it more susceptible to uranium extraction than the normal phosphate ore? It is possible that uranium in the leached zone may be present as adsorbed complexes or secondary phases. The following facts support this possibility and warrant the expansion of process control

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experimentation to test it.

1. The calcium uranyl phosphate autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ has been found in one locality.

2. The uranium present in the leached zone has been secondarily redistributed and probably oxidized. Under such conditions in many other deposits uranium has been readily fixed in the form of common salts-- phosphates, sulfates, carbonates.

3. Complexes of the type UO_4HPO_4 or $(\text{UO}_4)_3(\text{PO}_4)_2$ could be stable under the conditions of formation of wavellite. In fact, aluminum is used as a coprecipitant of uranium in nitrate solutions.

Were it not for the urgent nature of this third problem--the extraction of uranium from leached-zone rock--it would be logical to work first on determining the regional or areal mineralogic variation in the leached zone. However, it is immediately necessary to define the type of sampling that should be done by the groups, at Oak Ridge and elsewhere, which are engaged in process development studies. This problem has been discussed with Mr. Keith Brown and his associates at Oak Ridge and Dr. Marvin and his staff in Washington. The following approach has been proposed, with the approval of the above groups, and is now engaging our attention.

As it is impossible at present to select any particular sample or range of composition as typical of the leached zone, it is proposed that the extraction characteristics of polar or end-member types be studied in detail, both petrographically and metallurgically. The Trace Elements Section Washington Laboratory thus undertakes to furnish to Oak Ridge samples of two

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types -- (1) pseudowavellite-rich material, (2) wavellite-rich material. We shall also conduct separation and testing studies on these same materials, attempting thereby to see if their uranium can be concentrated by any petrographic laboratory techniques. In addition to the above, we shall furnish mineralogic and petrographic descriptions of any materials for which Oak Ridge has process development data.

Ultimately, it is hoped that a body of information can be built up with regard to the metallurgical characteristics of the principal lithologic constituents of the leached zone and that with this information as a control it may be possible to determine quickly by interpolation the metallurgical character of randomly selected samples.

These two problems will occupy most of the efforts of the mineralogists on Southeast phosphates during fiscal 1953, for which 4 man-years have been allotted. As time permits some work will be devoted to study of the paragenesis of the leached zone, continued mineralogic work on the lithologic zones of the land-pebble field, and further investigation on the occurrence of uranium in apatite by resumption of synthesis experiments and continued petrographic study of uranium in igneous apatite.

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