WAVELLITE SPHERULITES IN THE BONE VALLEY
FORMATION OF CENTRAL FLORIDA[1,2]

M. H. BERGENDAHL, *U. S. Geological Survey, Washington, D.C.*

ABSTRACT

Megascopic spherulitic aggregates of wavellite have been recently found in the Florida land-pebble phosphate field.

Petrographic studies were made to establish the identity of the mineral. Chemical and spectrographic data revealed the spherulites to be practically pure wavellite; the remainder is composed of phosphatic cement partly altered to wavellite.

The origin of wavellite is considered to be secondary, a replacement of apatite that has undergone ground-water leaching.

INTRODUCTION

An unusual occurrence of crystalline wavellite has been recently discovered in a sample taken from a phosphate prospect hole on the Royster tract, Sec. 14, T. 30 S., R. 25 E., in Polk County, Fla. The mineral was found in the leached zone of the Pliocene Bone Valley formation. Although clay-sized and barely visible wavellite has been described previously in the upper part of the Bone Valley formation (Altschuler and Boudreau, 1949), this mineral has never before been reported there as megascopic crystalline aggregates. The large size of the wavellite aggregates permitted isolation of the pure mineral for petrographic studies without the inconvenience of contamination by quartz sand or phosphate nodules.

GENERAL GEOLOGY

The rocks exposed within the Florida land-pebble phosphate field are considered by most writers to range from lower middle Miocene to Pleis-

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[1] This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

[2] Publication authorized by the Director, United States Geological Survey.

tocene age. All are thin, nearly flat-lying sediments. The oldest strati-
graphic unit is the Hawthorn formation of Miocene age, a fossiliferous
phosphatic limestone, interbedded with sand and clay. The Hawthorn
formation is overlain unconformably by the Pliocene Bone Valley forma-
tion, a karst topography having been developed on the Hawthorn during
late Miocene time. The Bone Valley formation is composed of two major
lithologic units: the lower, a bedded marine phosphorite, containing
phosphate nodules, quartz sand, and clay; and the upper, a leached zone,
a white to gray-brown clayey sand, cemented in places into porous
nodules and boulders by secondary phosphate, pseudowavellite, and
wavellite. Near the bottom of the leached zone, crumbly gray phosphate
pebbles are present. The lower part of the Bone Valley formation con-
stitutes the economic phosphate deposit of the land-pebble phosphate
field.

Cathcart and others consider the leached zone to have been formed
during the interval between post-Bone Valley and pre-Pleistocene inunda-
tion, during which time the phosphate deposits were exposed at the sur-
face. Downward-percolating ground water removed the soluble calcium
phosphate and redeposited aluminum phosphate. Channels were eroded
into the upper part of the Bone Valley formation before the encroach-
ment of Pleistocene seas.

Pleistocene deposition is represented by loose quartz sands which are
exposed at the surface throughout most of the land-pebble field.

More complete discussions of the geology may be found elsewhere
(Cathcart 1950; Altschuler and Boudreau 1949; Cathcart and Davidson
1952; Cooke 1945).

DESCRIPTION

The wavellite crystals are in the form of spherulitic aggregates ranging
in diameter from 1 mm. to 11 mm. Some individual spherulites attain
diameters of 9 mm. Both concentric and radial structures occur. Radial
structures are produced by the arrangement of individual bladed crystals
about a core or nucleus of short doubly terminated crystals, often of dif-
ferent orientation from the radiating crystals.

The spherulites are composed of several concentric layers of large
crystals. The cores of some spherulites consist of groups of feathery crys-
tals. Each layer of large radial crystals in a spherulite is separated from
the next by sheaves of bladed crystals which appear megascopically as a
concentric line (Fig. 1). These tiny sheaves fill interstices around the
outer edges of the larger crystals. Many of them seem to radiate about a
nucleus. The small size and concentric arrangement of these small ag-
gregates of crystals suggest an interruption of crystallization during the

growth of the spherulite caused possibly by a change of environmental conditions.

<center>PETROGRAPHY</center>

Indices of refraction which were determined from crushed fragments ($-100+120$ mesh) are as follows: α 1.52–1.53, β 1.53–1.54, γ 1.55. All
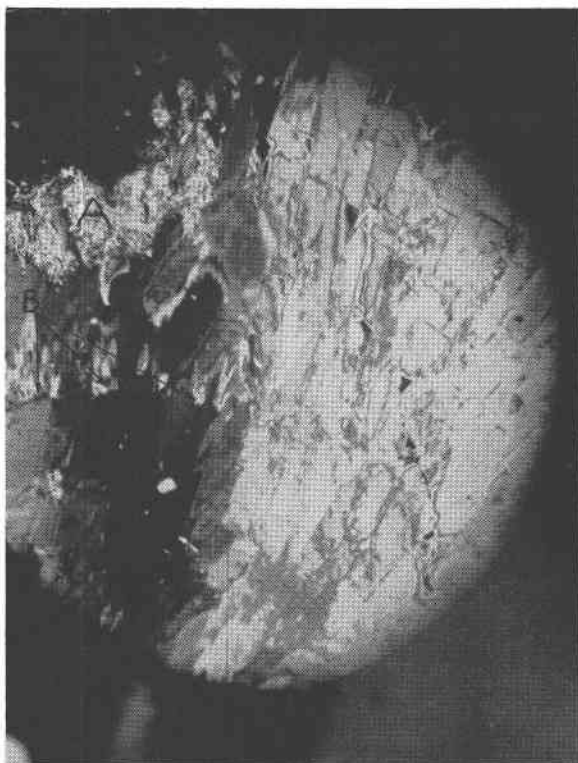

Fig. 1. Portion of spherulite showing radial arrangement of wavellite crystals. Part of concentric structure marked by cryptocrystalline sheaves of wavellite at B. Partly replaced phosphatic cement in upper left at A. Crossed nicols, $\times 70$.

crystals examined exhibited parallel extinction under crossed nicols (Fig. 2). The only distinguishable interference figure obtained was a centered optic axis figure, from which the positive characteristics of the mineral were determined. The dispersion was $r > v$, barely perceptible.

Five thin sections were made of individual spherulites and aggregates. All of these except one (Fig. 3) were almost pure wavellite. Figure 3 is a thin section made from a spherical aggregate of detrital quartz grains cemented by a network of microscopic wavellite rosettes. The spherical

form is due to the habit of wavellite crystal growth, radially in all dimensions about a central nucleus or core. All five thin sections reveal the presence of a brown secondary phosphatic cement (described by Altschuler and Boudreau, 1949) which forms an irregular thin coating around the spherulites and also lines cracks and fills interstices between wavellite
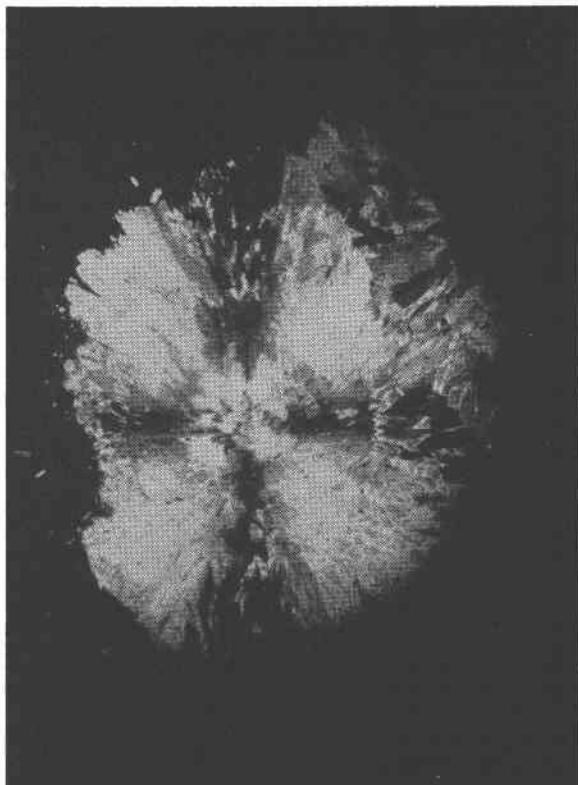

Fig. 2. Spherulite exhibiting extinction cross by radiating wavellite crystals. Crossed nicols, ×20.

crystals. Most thin sections show this phosphatic cement partly replaced by cryptocrystalline wavellite.

Mineralogy and Chemistry

Both chemical and spectrographic analyses (Tables 1 and 2) were made of the wavellite.

Using the formula for wavellite, $Al_6(F,OH)_6(PO_4)_4 \cdot 9H_2O$ (Winchell, 1951), the molecular percentages of Al_2O_3 and P_2O_5 were computed as
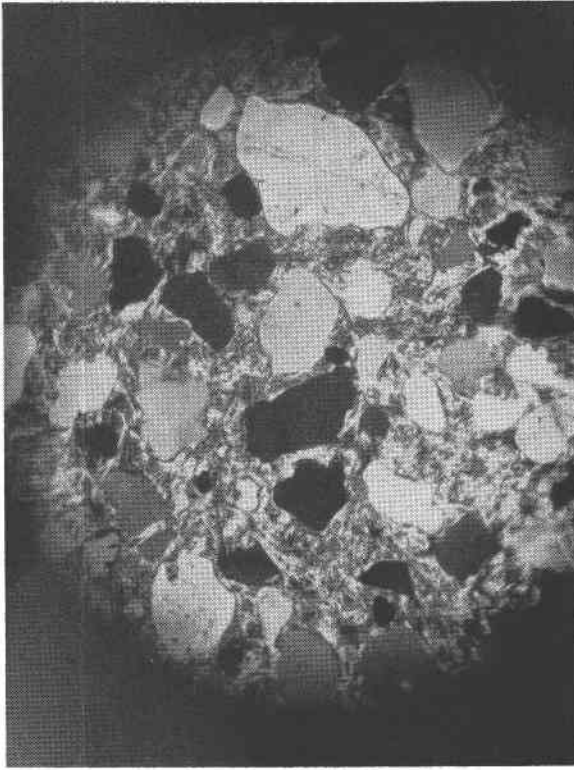
FIG. 3. Quartz grains cemented by cryptocrystalline wavellite. Section of a spherical aggregate. Crossed nicols, ×70.

TABLE 1. PARTIAL CHEMICAL ANALYSIS*

	Per Cent
Equivalent U	0.002
Al_2O_3	33.3
CaO	0.00
F	0.93
Fe	0.16
P_2O_5	33.0
SiO_2	1.62
U	0.003
Total	69.015

* Analysts: Alexander Sherwood, chemistry; B. A. McCall, radiation.

TABLE 2. SPECTROGRAPHIC ANALYSIS*

Elements	Per Cent
Al, P..	Over 10
....	1–10
Si..	0.1 – 1.0
Fe, Mg..	0.01 – 0.1
Sr, Cr, V, Ti...	0.001 – 0.01
....	0.0001– 0.001

* Analyst: Charles Annell.

38 per cent and 35.2 per cent, respectively. The formula for wavellite given in Dana's System of Mineralogy (Palache et al., 1951) is $Al_3(OH)_3$-$(PO_4)_2 \cdot 5H_2O$, with the constituents in the following percentages:

Al_2O_3	37.11
P_2O_5	34.47
H_2O	28.42
Total	100.00

Analyses of wavellite in Dana list Al_2O_3 from 31.01 to 37.44 per cent and P_2O_5 from 32.72 to 34.16 per cent. The chemical analysis (Table 1) lists Al_2O_3 as 33.3 per cent and P_2O_5 as 33.0 per cent, well within the limits of the analyses cited in Dana.

This departure of Al_2O_3 and P_2O_5 from the theoretical formula percentages can be explained. Altschuler states (written communication, Sept. 9, 1952) that small amounts of constituents not detectable spectrographically and not listed in the chemical analysis, or small amounts of one or more additional secondary hydrous aluminum phosphates, could alter the theoretical ratio of Al_2O_3 to P_2O_5, even though the sample is essentially pure wavellite. In addition, excess water could account for the P_2O_5 and Al_2O_3 deficiency.

The 1.62 per cent SiO_2 in Table 1 is assumed to be detrital quartz. Figure 3 shows that quartz is incorporated in some of the spherulites. The sample analyzed was composed of a number of spherulites, none of which were examined microscopically. It is not improbable that some detrital quartz could have been present in the sample. Fluorine can substitute for OH, and Fe may be present in small amounts in wavellite, substituting for Al_2O_3 (Altschuler and Boudreau, 1949). The absence of CaO in the analysis precludes the possibility that apatite, $Ca_5(F,Cl)P_3O_{12}$, or pseudowavellite, hydrous phosphate of Al and Ca, is present in the phosphatic cement. The chemistry and mineralogy of uranium in the leached zone are under study by others and are beyond the scope of this paper.

Origin and Significance

Altschuler and Boudreau (1949) have discussed the origin of wavellite. They state that wavellite is formed by the leaching action of ground water on apatite; CaO is removed in solution, and Al^{+++}, presumably introduced from clay minerals, combines with the P_2O_5 from apatite to form wavellite. Prior to leaching, the apatite was present as phosphate
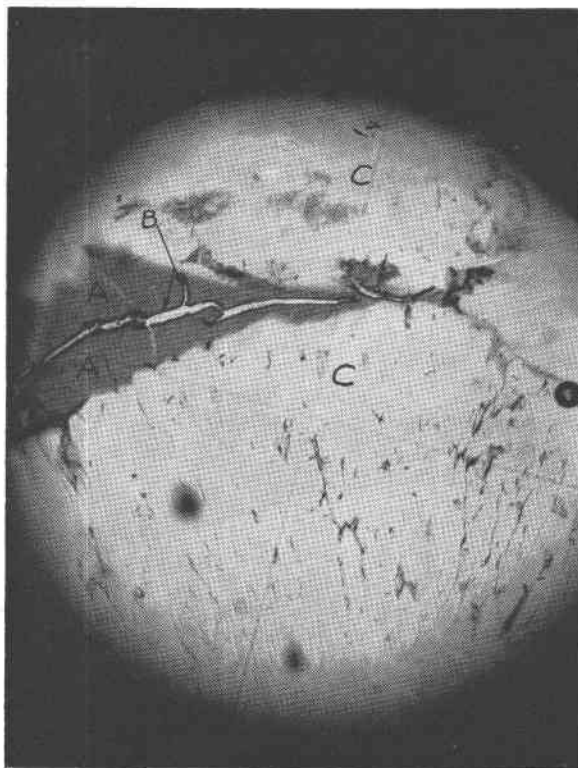

FIG. 4. Section of two spherulites with phosphatic cement filling space between them. Two generations of phosphatic cement line the cavity, the earlier (*A*) partly replaced by wavellite. The later generation (*B*) lines the large crack and fills small cracks and cavities in the earlier generation. The later phosphatic cement is darker. Wavellite crystals designated by *C*. Uncrossed nicols, ×70.

pebbles and possibly also as a primary cement. Leaching resulted in redeposition of a secondary cement or glazed phosphate composed of varying percentages of apatite, pseudowavellite, and wavellite.

Figure 4 shows two generations of phosphatic cement lining a cavity between two wavellite spherulites. The earlier generation is partly re-

placed by wavellite; the later coating lines the cavity and is unreplaced. It is apparent from these relationships that some phosphatic cement was deposited after the wavellite crystallization ceased. Possibly a rise in the water table was responsible for the later deposition.

It is reasonably evident that the development of the large wavellite spherulites was dependent on three conditions:

1. The presence of sufficient phosphatic cement or phosphate nodules to supply the necessary P_2O_5.

2. High permeability in the leached zone to permit adequate circulation of ground water and enable the growth of large crystals.

3. The proximity of clay minerals or some other source of Al_2O_3.

The chemical composition of the sample (Table 1) shows the absence of CaO, thus removing the possibility of pseudowavellite being present as an intermediate mineral in the alteration, and also the consideration of the brown phosphatic cement as apatite.

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