# THE MINERALOGY AND PARAGENESIS OF THE VARISCITE NODULES FROM NEAR FAIRFIELD, UTAH. PART 2

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# DESCRIPTION OF STRUCTURES AND THEIR INTERPRETATION

The Fairfield variscite and associated phosphates occur almost entirely in nodules. A small amount of the material is in angular fragments, probably breccia fragments of former nodules. The nodules range in size from a quarter of an inch to two feet or more in diameter; the commonest range of sizes is from one to three inches. They are generally spherical in form, some are flattened. A few show an interference in shape where two nodules grew into contact.

# RELATION OF NODULES TO ENCLOSING MATERIALS

Most of the nodules are enclosed in brown earthy limonite which contains abundant calcite disseminated through it. The calcite is probably residual from the original limestone. No limonite has been found inside any of the nodules, although in some the outer layer of pseudowavellite is slightly iron-stained. Moreover, the limonite tends to be concentrated around the phosphate nodules. If limonite had been present before the introduction of pseudowavellite, probably some of it would have seeped into the fractures in variscite later filled by pseudowavellite; such does not occur. Thus the limonite replaced the limestone and filled fractures in chert fragments after the phosphate minerals were deposited.

Many of the nodules have masses of chert attached to their surfaces. The chert is in angular fragments up to an inch across, very loosely held together, and with wide unfilled openings between many of the fragments. The brecciation of the chert must have preceded the formation of the nodules since the nodules commonly show very little fracturing while the chert surrounding them is badly shattered. Small crystals of calcite and aggregates of tiny quartz crystals grow upon the walls of the chert fragments. Limonite and small pseudowavellite nodules are cut by thin seams of coarse calcite and of fine quartz.

A few small nodules have been found embedded in angular fragments of gray alunite occurring mixed with angular fragments of chert. Others have angular fragments of alunite attached to their walls. Thus the alunite must have preceded the formation of the phosphates and the strong brecciation of the chert.

Within some of the nodules are large, angular fragments of black chert surrounded by thin pseudowavellite bands; the fragments are very slightly rounded at their corners, suggesting slight replacement. The masses containing these chert fragments are themselves highly brecciated, and may represent a mechanical mixture of chert and phosphate fragments (variscite at the time of brecciation).

Very thin black seams of fine quartz cutting variscite, and preceding the deposition of pseudowavellite (see later), are rare. One polished specimen, Fig. 1, is made up of small rounded, partly altered variscite nodules between which is found this same black quartz; it is definitely earlier than the alteration products of the variscite, but seems in part to have filled in between an aggregate of small variscite nodules, perhaps by replacement of calcite (limestone).

# GENERAL DISTRIBUTION OF THE MINERALS WITHIN THE NODULES

The general distribution of the minerals within the nodules has been described by Larsen and Shannon (1930b, pp. 308-309). Most of the nodules are formed of successive, locally separated shells of fibrous, finegrained, yellow pseudowavellite, inside of which is an irregular coating of granular porous aggregates of yellowish pseudowavellite; the central portions are generally hollow. Some nodules still contain cores of brilliant green variscite; these have fine, banded shells of pseudowavellite, commonly separated, as the outer material, inside of which is a white dense layer completely surrounding the variscite kernel. It is in the open lenticular spaces between the kernels and the outer yellow shells that the rare crystal-forming species are generally found. Through the green



FIG. 1. Photograph of a polished variscite nodule. The black seams are fine-grained quartz; the gray seams in the center of the nodule are a darker green variscite in a normal variscite. The white shell surrounding the variscite is a dense pseudowavellite; the outer finely-banded material is the early pseudowavellite.  $\times 1$ 

variscite kernels run occasional banded veinlets of pseudowavellite; many of the kernels contain isolated banded spherulites of pseudowavellite, or of wardite and millisite.

# DETAILED DESCRIPTION OF THE STRUCTURES AND THEIR SIGNIFICANCE

Below are given descriptions of the manner in which each mineral occurs in the nodules, and interpretation of its significance. Part is a repetition of the descriptions given by Larsen and Shannon. The minerals are taken up roughly in their order of decreasing abundance, which also roughly follows their sequence.

### Variscite

Variscite is the dominant mineral in many of the nodules and probably was the original mineral of all of them. It invariably occurs in the interior of the nodules as a massive, fine-grained, compact and rounded core; two or more residual kernels may occur in one nodule. Some variscite kernels are cut by fine seams, and surrounded by a thin band of darker green variscite (Fig. 1). This is probably due to a slight coarsening of grain around the periphery and along incipient cracks where accessibility to solutions was greater.

All the variscite seen in this study has a very fine and even grain size, about 0.01 mm. or less in diameter. Larsen and Shannon (1930b, p. 333) found coarser variscite as crystalline plates in the white powdery layer surrounding the green kernels; this was not seen by the writer.

There is no doubt but that the green variscite was the first mineral deposited. All the other minerals associated with it either replace it or occur in or on minerals which have replaced it. The coarser variscite found by Larsen and Shannon and mentioned above, probably recrystallized from residual variscite remaining after the replacement of variscite by white powdery pseudowavellite.

Some nodules have cores of variscite much smaller than the cavities they occupy, and not attached to the cavity walls at any point; these cores have very definitely been partially dissolved after the replacement by the outer pseudowavellite shells. This is evidenced both by their smallness in relation to the size of the cavities they occupy, and more definitely by the fact that small veinlets of pseudowavellite which formerly traversed the larger cores, now project outward from the surface of the variscite kernels into space as thin plates. Solutions with a selective solvent action, rather than a replacing action, must have dissolved the variscite, leaving the pseudowavellite unattacked. A precisely similar structure has been developed artificially by the use of a hot KOH solution on fragments of variscite containing pseudowavellite veinlets. This is discussed later.

It may be that the original variscite nodules were deposited as colloidal masses (gels), but only slight evidence supports this view. Some of the polished variscite displays discontinuous, anastimosing films of deeper green variscite, as noted above. Many of these healed cracks do not extend to the edges of the nodules, and may in part be due to internal tensional forces. Similar healed cracks in chert nodules are considered shrinkage cracks caused by a coarsening of a silica gel. Other evidences of colloidal origin are absent, unless fineness of grain and nodular form can be considered as such. Metacolloidal textures are in general absent from the variscite of other localities; some carry variscite crystals in vugs, as in the Arkansas deposit and the "lucinite" of Lucin, Utah. Banding is rarely seen, and is absent in the Fairfield variscite. It seems best to consider the variscite as deposited in the crystalline state in which it occurs at present.

### Pseudowavellite

Pseudowavellite is the most abundant phosphate mineral in the deposit, and makes up the bulk of most nodules. It occurs as thin, banded and simple shells and veinlets, of which some contain intergrown deltaite: as spherulitic aggregates; as banded spherules; as irregular to angular masses in variscite; and as pseudomorphs after gordonite.

The great majority of the nodules contains nothing but pseudowavellite, as tight-fitting, thin, yellow shells surrounding a central hollow core. Lining the walls of the central cavity are granular aggregates or spherules of pseudowavellite which in some nodules very nearly filled the cavity.

The nodules still containing variscite are completely surrounded by a layer, up to a centimeter thick, of banded pseudowavellite; a few carry outer bands which are fairly coarse grained and rudely spherulitic and which contain abundant deltaite intergrown with the yellow pseudowavellite. Such deltaite has been seen in only a few specimens. Generally, the outer bands are composed of subparallel or matted fibers of pseudowavellite, but some are coarse grained and vitreous. The various layers composing the outer shell of pseudowavellite are continuous around all, or a large part, of the nodule. Commonly veinlets up to a few millimeters wide cross the nodules; these veinlets are banded and their banding is continuous with the banding of the outer shell. Thus, they must have formed simultaneously. Many of the pseudowavellite veinlets have a central black line made up of fine-grained quartz; some of the sharp indentations and cusps of the outer yellow shells have a similar central line of quartz. The banding of the pseudowavellite is symmetrical on either side of these veinlets. The original variscite must have been fractured, and fine-grained quartz deposited in the tiny openings. These fine veinlets of quartz gave access to the replacing pseudowavellite solutions, and it was along and outward from these veinlets that the early pseudowavellite was deposited. Figure 1 shows these black quartz veinlets upon which, in part, the pseudowavellite has centered. In nodules in which the original fracturing made a breccia of the whole mass, the introduced quartz formed a "boxwork" upon which banded pseudowavellite deposited; in a few specimens the central part of each "box" is hollow, giving a honey-comb effect to the pseudowavellite. In a few of the "boxes" are small residual cores of variscite. These have formed in a manner identical to the boxwork of wardite and millisite, built up on fine pseudowavellite veinlets, and described below. It serves to indicate further the replacement character of the pseudowavellite.

Small banded spherules and lenses of yellow pseudowavellite occur in the variscite. Some of these are isolated, but others occur as bulges along fine pseudowavellite veinlets. The veinlets along which they developed are offshoots from the main outer pseudowavellite bands, and the sequence of the banding in them is similar to that in the outer bands; thus these are related to the early pseudowavellite.

Inside the outer shell of pseudowavellite is commonly a discontinuous band, or shell, of wardite and millisite, either in colloform bands or spherules; the spherules commonly grow into open cavities toward the center of the nodule. Beyond the wardite-millisite band, and commonly separated from it by a discontinuous irregular cavity, is another shell of dense yellow roughly banded pseudowavellite completely enclosing the variscite core. Veinlets from the outer pseudowavellite shells cut the inner dense pseudowavellite shell; but commonly the inner shell contributes locally toward the veinlet. Thus the veinlet is made up of initially banded pseudowavellite, the bands of which are continuous with the bands of the outer shell, and on either side of these are additional bands of more dense pseudowavellite continuous with the bands of the inner shell of the mineral. Thus the veinlet must have been there before the inner pseudowavellite bands were deposited.

In a few specimens the inner layer of pseudowavellite is made up of thin, slightly separated, successive shells, separated as though through shrinkage. However, each shell follows very faithfully the outline of the shell preceding and succeeding it. Moreover, the width of separation of two successive shells is very constant over considerable areas and even around sharp turns. The shells clearly have been formed by replacement of the variscite, so that the reasonable explanation of their separation is to assume a period of variscite solution between successive periods of replacement to form the shells, rather than considering it a shrinkage (colloidal) phenomenon. There is ample evidence elsewhere to prove that variscite was removed by solution at one or more times during the mineralization. Very finely fibrous, white, powdery pseudowavellite forms a thin coating over these separated shells.

Many of the variscite kernels are completely surrounded by a tightfitting, white, chalky layer of pseudowavellite (deltaite?), about a millimeter or more thick. This layer generally ends sharply against the variscite, but in places the contact with the variscite is gradational and irregular, indicating replacement of the variscite rather than a coating. In a few specimens a white, powdery layer of pseudowavellite coats variscite and separated shells of pseudowavellite, and occurs irregularly on many of the crystal-forming minerals occurring in the cavities. It is later in the sequence than most, if not all, of the minerals in the nodules. A similar late pseudowavellite occurs as tiny isolated oolites perched upon late cavity minerals.

Pseudomorphs of pseudowavellite after gordonite have been seen in two specimens. In one, a group of gordonite crystals has been completely replaced by a porous aggregate of pseudowavellite. Other gordonite crystals have been replaced by a very fine-grained, white pseudowavellite, leaving well-formed but fragile pseudomorphs.

### Wardite-Millisite

Wardite and millisite nearly always occur together in the nodules; they comprise the gray banded layers and spherules, the blue to gray crystalline crusts, and white, coarse-grained masses near tan pseudowavellite. They occur as successive alternating layers of gray to white, dense millisite and pale blue to colorless vitreous layers and crusts of wardite. In general, the centers of the spherulites and the earlier bands of the banded forms are made up mostly of millisite, while the proportion of wardite increases considerably away from the centers and the earlier bands.

Many of the variscite kernels contain spherules of wardite and millisite up to a centimeter in diameter. Some are perfectly round, isolated forms in a broad field of variscite, but more commonly they occur sparsely distributed along cracks in the variscite, and many of these appear to have been offset by micro-faulting. Some may have been offset by such a movement, but most have formed as two separate half spherules from separate centers on either side of the fracture, and never represented a single complete spherule. This is shown by the fact that the bands in the spherules, when they approach the crack, turn slightly and tend to follow the crack, thus indicating that the crack influenced their original form. Moreover, there seems to be no case in which there is any evidence of microscopic brecciation or lack of fit on opposite walls of the crack. A few of the offset spherulites are veined by vitreous yellow pseudowavellite, and are completely surrounded by a thin band of dense pseudowavellite; the vitreous material is earlier than the spherulites, and the dense material later, as is indicated by other structures in the same specimens. Figure 2 shows wardite-millisite spherulites veined and surrounded in this way. Some spherules center upon the walls of pseudowavellite veinlets and project outward as hemispherical forms into what was orginally



FIG. 2. Photograph showing small wardite-millisite spherules cut by a very thin veinlet of pseudowavellite and surrounded by pseudowavellite. The bands of the spherules tongue out when they meet the thin veinlet.  $\times 2$ .

FIG. 3. Photograph of delicate banding of wardite and millisite. The inward protru sions of the bands in places follow veinlets of pseudowavellite. Offsetting in the banding is not due to fracturing after formation of the bands.  $\times 2$ .

variscite. The pseudowavellite veinlets upon which the spherules are centered are in all cases continuous with the outer, early, banded shells of pseudowavellite, and the more dense pseudowavellite which surrounds the spherulites in all cases is continuous with the inner, more dense shell of pseudowavellite. Many of the spherules and hemispherules have coalesced where they grew together, and form scalloped, continuous bands around a number of centers.

Alternating layers of wardite and millisite form angular and waving bands immediately inside the outer pseudowavellite shell (Fig. 3). The angular banding in general conforms to the surface of the pseudowavellite on which it grew, while the wavy bands represent coalesced hemispherules whose closely spaced centers lie upon the pseudowavellite surface. Abrupt inward protrusions of the wardite-millisite banding is more or less symmetrical on either side of a central line, made up either of a thin veinlet of vitreous pseudowavellite or wardite, or in some, an indefinite preexisting crack. These pseudowavellite veinlets have banding continuous with the banding of the outer, earlier pseudowavellite, and continue inward toward the center of the nodule, completely crossing the wardite-millisite bands, then crossing an interior shell of dense yellow pseudowavellite and on into the variscite core. Some wardite-millisite shells are separated from the interior dense pseudowavellite by an open space, across which the pseudowavellite veinlets continue, and into which wardite crystals project. These veinlets are very definitely antecedent to the wardite and millisite bands, and to the dense pseudowavellite. The sharp inward protrusions of the alternating bands of wardite and millisite are without doubt controlled by the pseudowavellite veinlets upon which they are centered. Moreover, the dense inner pseudowavellite locally replaces the wardite-millisite bands in irregular protrusions and discontinuous veinlets near their contacts, and thus formed after the wardite and millisite. All the banded material in such structures must have formed by successive centripetal replacement of the original variscite. The sequence of mineralization shown by such specimens is: replacement of the variscite by the pseudowavellite to form the outer shell and, along fractures, to form the small veinlets; alternating replacement, by wardite and millisite, of the new surface of the variscite; some variscite was removed faster than the wardite and millisite were deposited, and into the resulting cavities grew crystals of wardite, some coated by millisite. Then the dense yellow pseudowavellite partially replaced the variscite kernel to form a shell surrounding it, and veining both the wardite-millisite bands and the variscite. This pseudowavellite is of the same generation as that surrounding the isolated spherules of wardite and millisite.

The colloform banding so beautifully developed by wardite and millisite seems not to be a colloidal phenomenon (metacolloid). Although the millisite occurs as fine fibers, the wardite bands are made up of relatively coarse, elongated subparallel grains, many of them terminating in recognizable crystal faces, and upon which grew the succeeding layer of millisite. The only phenomena suggesting an original gelatinous state are the repeated fine banding and the wavy nature of the banding, but neither of these requires diffusion through a gel (Liesegang rings) for their development. The repeated banding is generally developed on a microscopic scale, but in many specimens outer bands are developed several millimeters thick and made up of well-formed crystals of this order of magnitude which without doubt grew in open spaces. The wavy nature of the banding is commonly controlled by the wavy nature of the surface on which it grew, and the banding is generally not wavy when the surface on which it developed is straight, unless it started as a succession of independent spherules. The banded and spherulitic wardite and millisite must have been deposited from solutions largely by replacement of variscite, and in part in cavities.

Some large specimens are composed in greatest part of wardite. These specimens are cut by crossing thin veinlets of banded pseudowavellite forming an angular boxwork of the whole specimen. The "boxes" formed by the pseudowavellite veinlets are filled mostly with wardite. Parallel and next to the veinlets are alternate bands of wardite and millisite; away from the veinlets the wardite becomes the sole mineral, and occurs in coarse grains. In the center of each "box" is an open space and into this protrude crystals of wardite. Rarely a "box" shows a small kernel of variscite occupying part of its hollow core, and this kernel has a shell of pseudowavellite (in one case, with a thin band of deltaite) around it. Such boxwork specimens must have originated in this way: a variscite nodule was brecciated; in and along the fractures thus developed was deposited a boxwork of pseudowavellite veinlets; later solutions following these veinlets replaced the variscite with wardite and millisite bands parallel to the veinlets; slowly changing solutions stopped depositing millisite and started dissolving variscite faster than they deposited wardite, leaving a cavity to mark the center of each of the former brecciated fragments of variscite; into these cavities grew wardite crystals. The still remaining small variscite kernels were then partially replaced by pseudowavellite. This gives independently a sequence identical with that noted just above.

Other wardite specimens are similarly criss-crossed by pseudowavellite veinlets to form a boxwork; but in these the wardite (and millisite in small amounts) forms large banded spherules partly filling the interspaces between the pseudowavellite veinlets. Some of the spherules have their centers on the veinlets, but many complete spherules are supported only on neighboring spherules and the point of support is outward from the center of each. To form thus, the spherules must have started their growth in some supporting medium. It is believed these specimens represent variscite nodules which were brecciated, and the resultant cracks were filled with, and localized the replacement by, pseudowavellite to

form the pseudowavellite boxwork. Spherules of wardite and millisite started to develop in the variscite with their centers randomly placed; with time the variscite was removed faster than the wardite was introduced, leaving an aggregate of spherules, some probably loose, taking the space of the original brecciated fragment. Further introduction of wardite increased the size of the spherules, developed crystal faces on their surfaces, and cemented neighboring spherules together. It is certain that the wardite spherules are later than the pseudowavellite veinlets, and that there was originally a matrix material at least for the pseudowavellite to form in. The pseudowavellite commonly occurs as plates traversing open spaces between spherules; it must originally have had walls to determine its plate-like shape. In some instances where the pseudowavellite veinlet crosses a spherule, the pseudowavellite has been partially replaced leaving only discontinuous elongated patches arranged in line with the unreplaced parts of the veinlet. Variscite is the only mineral which can reasonably be considered as the original matrix material for the spherules, and the original walls for the pseudowavellite veinlets.

One fragment of a nodule is made up of a large mass of white, massive wardite and a massive buff-colored pseudowavellite, and the two are sharply separated by a purplish-brown layer of dense pseudowavellite. The relations of the wardite and pseudowavellite are not shown, nor is anything known of the nature of the nodule from which the fragment came.

## Deltaite

Deltaite is nearly as variable in its appearance and manner of occurrence as is pseudowavellite. Five distinct varieties and modes of occurrence were seen by the writer: minute triangular prisms in vitreous pseudowavellite; lavender crystals in cavities; massive lavender bands; dense gray bands; and minute yellow and colorless crystals on pseudowavellite.

In some of the early vitreous pseudowavellite bands and veinlets minute trigonal prisms of deltaite occur intergrown with the pseudowavellite, and evenly distributed through it. It is probable from their occurrence that the two minerals crystallized together. Pseudowavellite and deltaite have been shown in a previous section to be, probably, an isomorphous series, on the basis of Larsen and Shannon's published analyses (1930b); it is difficult to conceive how two members of such a series could occur thus intergrown, with sharp non-gradational boundaries. The two minerals are near the two ends of an isomorphous (?) series.

The occurrence of the lavender crystals of deltaite has been described

in the section on Descriptive Mineralogy. This deltaite is later than the outer pseudowavellite shell, and formed after the removal by solution of the original variscite kernel.

Massive bands of fine to medium grained lavender or powder-blue deltaite are optically identical with the lavender crystals. These bands generally occur inside the principal shell of pseudowavellite, and reach a thickness of five or more millimeters. They commonly form the innermost shell, and have crystalline crusts growing upon them extending into the central cavity. Some of these bands are discontinuous and appear to have replaced pseudowavellite, since the same band may change more or less abruptly from deltaite to pseudowavellite, or the deltaite may transect a pseudowavellite band. Although not certain, it seems probable that these deltaite bands followed the deposition of wardite and millisite.

One nodule contains dense gray bands a few millimeters wide, forming crossing veinlets in variscite such that the variscite is in angular to rounded blocks completely surrounded by the gray bands. The gray bands are made up of matted fibers of deltaite ( $\omega = 1.630$ ) with repeated thin bands of vitreous wardite in them. The nodule has an outer shell of banded pseudowavellite which must have preceded the formation of the deltaite and pseudowavellite. Dense yellow pseudowavellite occurs as an irregular band in the variscite immediately adjacent to the gray deltaite veinlets; the contact between the pseudowavellite and variscite is gradational, with irregular patches of the pseudowavellite extending into the variscite in a manner requiring replacement as its origin. This deltaite and wardite must have been deposited after the outer shells of pseudowavellite and before the pseudowavellite now seen surrounding the variscite. It thus was introduced at about the time the wardite and millisite were being deposited in other nodules. Apparently some local condition caused deltaite to form instead of the usual millisite.

Minute yellow and colorless crystals of deltaite occur lining cavities between bands of pseudowavellite; in some of these cavities are found small crystals of lewistonite, apparently resting upon the deltaite crystals

### Lehiite

Lehiite forms discontinuous dense gray bands and lenses inside the outer pseudowavellite shells. It commonly contains scattered parallel bands of relatively coarse wardite within it. It appears to have the same place in the sequence as the alternating bands of wardite and millisite. In general, the lehiite has formed chiefly by replacement of the variscite after the early pseudowavellite; part may have formed in open spaces, but no open spaces are present now to indicate this. Between the lehiite bands and the variscite cores run thin dense bands of pseudowavellite, and occasionally coarse gordonite plates. It thus must have formed after the early pseudowavellite and before the inner band of pseudowavellite, separating it from the variscite, and before the gordonite. In one nodule containing lehiite in a large lenticular band, wardite and millisite occur as spherules showing the same time relations as the lehiite: formed after the early pseudowavellite, but surrounded by a later pseudowavellite and gordonite.

## Gordonite

Gordonite nearly always occurs as coarse crystals in subparallel groups in the cavities between variscite and the pseudowavellite shells. Thin bands of coarse, subparallel aggregates separate variscite cores from surrounding pseudowavellite. Some fine-grained, platy, green gordonite coats variscite kernels in a thin layer, giving a velvety appearance to the surface.

Occasionally what appear to be single individuals occur in the cavities, and these crystals have a shorter prismatic habit than those occurring in aggregates. Very small single crystals of gordonite occur perched upon the inside walls of some of the granular rough shells of pseudowavellite, surrounding but separated from the variscite kernels. Gordonite has been found only in nodules which still contain variscite, and it is upon or near the variscite that it always forms. Frequently the gordonite crystals are attached to wardite crusts and extend inward toward the variscite kernels.

Bands of coarse plates in subparallel arrangement are present surrounding and replacing variscite kernels immediately inside the white or yellow late crusts of pseudowavellite. These are very similar to bands of montgomeryite surrounding variscite, and like montgomeryite the bands show crystals developed wherever open spaces have been available. The gordonite is thus later than all of the banded pseudowavellite.

Yellow granular oolites of pseudowavellite occur perched upon gordonite crystals and in one specimen have formed pseudomorphs after gordonite. White powdery layers of pseudowavellite likewise coat some of the crystals. In one small nodule a fairly heavy layer of a white amorphous material, probably related to pseudowavellite, fills in around gordonite crystals, and shows shrinkage cracks identical with mud cracks. Members of the apatite group occur as isolated crystals, needles, or aggregates on some of the crystals.

#### Englishite

Englishite most commonly occurs as subparallel aggregates of plates surrounding spherules of wardite and millisite in variscite; it has replaced both the wardite and the variscite. Likewise it forms aggregates of plates replacing variscite adjacent to bands of wardite and millisite. In cavities between wardite crusts and variscite kernels it occurs perched upon the wardite as subparallel aggregates of plates in irregular forms several millimeters across. One nodule contains a curved worm-like mass of englishite more than a centimeter long and several millimeters in diameter, growing on a crust of wardite.

Englishite generally occurs in the same nodules with montgomeryite and appears to be the earlier of the two; in one specimen a band of montgomeryite plates has been introduced into the variscite along what must originally have been the contact between a band of englishite plates and variscite. Members of the apatite group occur perched upon englishite in some of the cavities. The relation of englishite to the other crystallized species is not shown.

Englishite must have formed after the bands of pseudowavellite, the wardite and millisite, and the development of the open spaces by solution of the variscite. It is earlier than the montgomeryite and the crystallized apatite members.

#### Montgomeryite

Montgomeryite most commonly occurs as a thin band, made up of coarse subparallel plates, surrounding and replacing variscite, immediately inside white or dense yellow pseudowavellite. Where these bands project into open spaces, crystals of montgomeryite have developed. Commonly montgomeryite forms a similar thin band in variscite surrounding wardite-millisite spherules. Frequently it is associated with englishite, and has been formed after the englishite as a later band, or as crystals in cavities near englishite masses.

In cavities montgomeryite invariably forms crystals, some up to several millimeters long, and in aggregates a centimeter or more across. It usually forms as subparallel groups. Although it occurs in nodules which contain gordonite, its sequential relation to gordonite is not shown; the two minerals have not been found in contact. It occurs as crystals perched upon wardite crusts, and very commonly on the thin white or yellow separated shells of pseudowavellite near variscite. Occasionally needles and aggregates of apatite minerals and yellow granules of pseudowavellite are found resting upon the montgomeryite crystals.

### Overite

Overite is one of the rarest of the minerals in the nodules. In all but one specimen it occurs as coarse to fine crystals growing in cavities upon or near variscite; in one specimen it forms a band of subparallel plates. It is found growing upon spherulitic shells of pseudowavellite, and isolated or aggregated tiny oolites of nearly white pseudowavellite in turn grow on the overite.

A white fibrous radial group of some apatite member was found upon the tip of one overite crystal. Where overite is massive, it forms a thin shell of subparallel coarse plates between variscite kernels and the encrusting pseudowavellite, similar in occurrence to montgomeryite and gordonite. It is thus later than all the bands of pseudowavellite.

# Sterrettite

Sterrettite always occurs as single crystals growing from the walls of irregular cavities in a porous tan-colored pseudowavellite. Associated with it in the cavities are tiny crystals of an apatite mineral; generally the relations of the two are not seen, but occasionally the apatite grows upon sterrettite crystals.

The pseudowavellite containing these crystals is unusual in that none of it has the typical yellow color, but is buff to purplish-brown. The outer shells are very fine grained and compact, while the inner part of the nodules are made up entirely of compactly-grown, platy to fibrous spherulites of pseudowavellite; between the outer shells and the more porous core is commonly an open space, filled in part by loose aggregates of coarse pseudowavellite spherules or by large white spherules of wardite, with little or no millisite. It is in the opening between the outer shells and the core that many of the sterrettite crystals grow, although they can be found scattered through the cores in irregular small cavities.

All of the tan colored pseudowavellite of this type, containing sterrettite, occurred in the deposit in one small area somewhat removed horizontally from the main zone of mineralization. It is in specimens from this one area alone that sterrettite has been found.

#### A patite members.

In appearance and optical properties the members of the apatite group are extremely variable. Their habit variation is as follows: (1) balls of radiating fibers or prisms, (2) sheaf-like groups of needles, (3) subparallel aggregates of broad hexagonal prisms, (4) isolated hexagonal prisms, both elongated and stubby, and (5) irregular fibrous aggregates.

With the exception of one form of dehrnite, the apatite members are later than all the minerals closely associated with them in the nodules: they line cavities in pseudowavellite, lehiite, and chert; they are perched upon crystals of wardite, deltaite, gordonite, montgomeryite and sterrettite. The only exception is a shell of radially fibrous dehrnite about two millimeters thick lying between a shell of banded wardite and millisite and an inner shell of dense yellow pseudowavellite; this material seems

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definitely to have preceded the inner pseudowavellite. The dehrnite must have formed in an opening between the wardite layer and variscite, since the dehrnite is separated from the wardite by discontinuous lenticular openings.

It seems probable that, in general, the apatite members were the last phase of the mineralization of the nodules. The considerable variation in the types of material deposited in this last phase suggests a complex history; that strictly local conditions were not the principal factor controlling what type of apatite member was deposited is indicated by the fact that as many as three different types occur in the same nodule, and that individual types are frequently zoned.

The detailed sequence of the members within this group has not been determined since the chemistry of the various types is incompletely known. Most of the types are present in quantities far too small for chemical analysis.

#### SEQUENCE OF MINERALS

The sequence of deposition of the phosphate minerals has for the most part been definitely determined.

Variscite without doubt was the original phosphate mineral to be deposited; in itself it represents a complete stage of deposition, and shows no alternations or gradational sequence with any other mineral: all of the variscite was deposited before any other phosphate started to form.

Pseudowavellite was the second mineral to form in the nodules, and represents here a centripetal replacement of the original variscite. Accompanying the earliest pseudowavellite was a small amount of deltaite.

Millisite and wardite directly follow pseudowavellite in the sequence. The two were alternately deposited as successive bands or shells; most of the millisite is earlier than most of the wardite, although wardite accompanied the earliest millisite, and millisite accompanied the latest wardite. The earlier material all represents replacement of variscite, while much of the later wardite was deposited in open spaces.

Lenticular crusts of dennisonite containing thin bands of wardite, and veins and bands of gray deltaite containing thin bands of wardite occupy positions in the sequence identical with millisite; no two of the three types ever occur in contact in the same nodules so that their relative sequence cannot be told. Since they are all interbanded with wardite, it may be that they all formed simultaneously, local conditions determining which was to deposit.

Following the wardite (and gray deltaite and lehiite) is a recurrence of pseudowavellite, forming compact yellow and white layers surrounding the remaining variscite. Most of this material is likewise a replacement of the variscite. In one nodule, a band of dehrnite, deposited in part in openings, must have formed between the wardite and the second pseudowavellite periods.

Some deltaite, particularly the massive lavender material, either accompanied the second stage of pseudowavellite, or followed it by replacement; the crystalline deltaite must have formed at this same time.



The minerals following the second pseudowavellite stage commonly occur as crystals in cavities of the preceding minerals. The mutual relations of the minerals of this group are poorly known since the minerals are rare and when found are not ordinarily accompanied by other members of the same group. Certain relations are shown however: englishite

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is earlier than montgomeryite, and probably follows gordonite; the apatite minerals are later than the other crystallized minerals. Overite and sterrettite have not been found with crystalline types other than the apatite members, so they remain unplaced in the sequence of this group.

Isolated oolites of yellow to white pseudowavellite were deposited after and upon the crystal-forming minerals, with the exception of the apatite members; at least some of the apatite minerals were later than these pseudowavellite oolites.

Figure 4 gives a tabulation of the sequence. Five distinct stages are represented: (1) the original variscite; (2) the banded minerals which replaced and enclosed the variscite; (3) the crystal-forming minerals in cavities of the earlier minerals; (4) the minor reversion to pseudowavellite; (5) members of the apatite group, overlapping perhaps with (4).

Minerals other than phosphates associated with the nodules are in most part either earlier or later than the phosphates. The one exception to this is the fine-grained quartz which occurs as tiny black veinlets in the variscite, and along which the banded pseudowavellite has formed; this quartz represents the first mineral to form after variscite.

Alunite and chert preceded the phosphates, and are probably genetically unrelated to them. Limonite is very probably later than the phosphates. Late calcite and quartz in tiny seams and crystalline coatings are later than any of the phosphates and the limonite.

### CHEMICAL SEQUENCE

The mineralogical sequence has been shown to represent five distinct stages of solution activity. Each of the stages displays unique chemical qualities.

Stage 1. The primary stage is the deposition of variscite. Mineralogically this is simple and represents the deposition, from moving phosphatebearing waters, of a normal hydrous aluminum phosphate—Al(PO<sub>4</sub>) ·2H<sub>2</sub>O. No other material was deposited at this stage.

Stage 2. This period represents an alteration of the variscite, an alteration which was largely a readjustment of the original aluminum phosphate and the introduction of CaO, rather than a bulk replacement of the variscite by entirely new material. During this time hydrous basic phosphates of aluminum and calcium, together with some sodium, encroached upon the variscite. The chief minerals of this stage, pseudowavellite, wardite, and millisite, have an atomic ratio Al: P (or PO<sub>4</sub>) = 3:2. The time sequence of all the minerals of the stage closely parallels an increase in the atomic ratio of Na:Ca, with a reversion at the end. The following tabulation demonstrates this fact:

			Na:Ca
Early	Pseudowavellite	$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$	0:1
	(Deltaite	$Ca_2Al_2(PO_4)_2(OH)_4 \cdot H_2O$	0:1)
	(Lehiite	Ca <sub>5</sub> Na <sub>2</sub> Al <sub>8</sub> (PO <sub>4</sub> ) <sub>8</sub> (OH) <sub>12</sub> · 6H <sub>2</sub> O	2:5)
	Millisite	Ca <sub>2</sub> Na <sub>2</sub> Al <sub>12</sub> (PO <sub>4</sub> ) <sub>8</sub> (OH) <sub>18</sub> · 8H <sub>2</sub> O	1:1
	Wardite	$CaNa_4Al_{12}(PO_4)_8(OH)_{18} \cdot 8H_2O$	4:1
	Pseudowavellite	CaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> · H <sub>2</sub> O	0:1
Late	Deltaite	$Ca_2AI_2(PO_4)_2(OH)_4 \cdot H_2O$	0:1

Although millisite and wardite were deposited alternately, the bulk of the millisite crystallized before the bulk of the wardite.

The minerals of this group are the most basic of the series; the ratio of PO<sub>4</sub>:OH is approximately 2:5, as compared to 1:1 in the third group. This is the principal group in which alkalies are important. Dehrnite occupies an anomalous position late in this group.

Stage 3. Although the actual sequence of the minerals in this group could not be definitely established, the minerals as a whole show certain distinct chemical characteristics. The atomic ratio of Al: P (or PO<sub>4</sub>) is approximately 1:1 in all cases, a decrease in the relative amount of Al from stage 2. The minerals of this group are all basic, the ratio of the radicals (PO<sub>4</sub>): (OH) approximating 1:1; this is a marked decrease in hydroxyl content from stage 2. The water of crystallization is somewhat higher in stage 3, so that the total water for the minerals of both groups is about the same.

Gordonite occupies a rather anomalous position in this mineral association. It is the only mineral in the deposit in which MgO is dominant, yet it was apparently formed in the same stage with minerals containing no determinable MgO. The minerals of the preceding and succeeding stages all contain MgO as a minor constituent (analyses, Larsen and Shannon, 1930b). Although there is no evidence from its occurrence, gordonite might be considered as having formed in a stage of deposition intermediate between stages 2 and 3. It is by far the most abundant of the stage 3 minerals.

Stage 4. This period represents a reversion to early conditions with the deposition of minor amounts of pseudowavellite, which was apparently deposited from solution rather than being a reaction product of the variscite. Part is certainly earlier than the apatite group, but some may be later.

Stage 5. This stage is represented solely by minerals belonging to the apatite group. Although analyses are not available for most of the minerals of the group, it can be said with some certainty that they are characterized by the absence of essential  $Al_2O_3$ . From the analyses available (Larsen and Shannon, 1930b) it seems that the variation within the group is in the relative quantities of Na<sub>2</sub>O, K<sub>2</sub>O, CaO, and MgO and, to some

extent,  $H_2O$  and  $CO_2$ . What the sequence of this variation may be is not known. There were probably several periods of crystallization within this stage since two or more members occur together in the same nodule.



FIG. 5. Ternary diagram on which is plotted the atomic ratios Ca+alkalies:Al:OH of the analyzed minerals from the nodules. 1 variscite, 2 pseudowavellite, 3 deltaite, 4 millisite, 5 wardite, 6 lehiite, 7 dennisonite, 8 gordonite, 9 englishite, 10 montgomeryite, 11 overite, 12 sterrettite, 13 lewistonite, 14 dehrnite.

The chemical characteristics of the stages can be seen in Figs. 5 and 6. In Fig. 5, the ratio Ca+alkalies: Al:OH is plotted for each phosphate mineral found in the deposit; the points above the broken line (more basic minerals) represent only minerals formed in stage 2; those below the line are stage 3 minerals (with the exception of variscite). Figure 6 shows the ratios of Ca+alkalies: Al: PO<sub>4</sub> of the same minerals; in this the dotted line likewise divides stage 2 from stage 3 minerals. In both diagrams, the two analyzed apatite minerals (stage 5) are isolated to the left, the only minerals free of essential Al<sub>2</sub>O<sub>3</sub>.

Limonite was apparently the last to be deposited in abundance, and

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would seem to have no genetic relation to the minerals of the nodules. It has not replaced or altered any of the phosphates, and is not included in any of the nodules.



FIG. 6. Ternary diagram on which is plotted the atomic ratios  $Ca+alkalies:Al:PO_4$  of the analyzed minerals from the nodules. 1 variscite, 2 pseudowavellite, 3 deltaite, 4 millisite, 5 wardite, 6 lehiite, 7 dennisonite, 8 gordonite, 9 englishite, 10 montgomeryite, 11 overite, 12 sterrettite, 13 lewistonite, 14 dehrnite.

In the discussion of these stages of deposition, no recognition has been given to the presence of quartz or calcite in the nodules. Calcite is not common in the nodules, although it is common on their outer surfaces. Where it formed it was definitely later than the banded vuggy material containing it; most of it is probably later than all the phosphates. The fine seams of quartz associated with some of the veins of pseudowavellite formed during the phosphate period. They are believed to be an intermediate and brief interlude in the sequence of the phosphates, and were probably associated in some way with the movements which fractured the variscite and preceded stage 2.

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#### Periods of Phosphate Deposition

It has been shown that the variscite was the first mineral to be deposited, and that the principal later minerals formed by alteration and replacement of the variscite. It seems, therefore, that two major periods of mineralization can be postulated: the first period represents the deposition of variscite from phosphate-bearing solutions; the second period represents primarily an alteration of the original variscite, and not the introduction of new phosphate material, since the alteration minerals are found associated only with variscite or where variscite must originally have been. Thus the solutions which deposited the variscite need have no relation in time to the solutions responsible for the alteration minerals. Actually a time interval between the two periods is indicated by the fact that after all of the variscite had been deposited, movements causing brecciation and fracturing of the variscite took place, and this preceded all of the secondary phosphates; the length of the interval between the two periods is not indicated, but need not have been long.

## STRUCTURAL HISTORY OF THE NODULES

A cursory examination of many of the nodules suggests several periods of fracturing, or movement along pre-existing fractures, during the development of the secondary phosphates. Many structures appear to be offset: wardite-millisite spherulites and bands do not meet on opposite sides of a fracture; white pseudowavellite areas are in contact with variscite along sharp straight breaks; inner bands of pseudowavellite appear offset against veinlets of pseudowavellite.

When studied in detail, it is necessary to conclude that only one period of fracturing and movement occurred during the phosphate mineralization, and that this took place after the formation of the variscite and before any of the alteration products. There is no doubt that the outer shell of pseudowavellite was the first mineral to replace the variscite, and these outer shells are always intact. Moreover, the veins of pseudowavellite crossing the nodules have banding continuous with the banding of the outer shell, and thus were formed simultaneously with the outer shell; these are not displaced or offset by fracturing. Many fractured nodules have a continuous outer pseudowavellite shell separated from the variscite core by a wide, almost continuous cavity; the rounded core is made up of angular blocks of variscite in contact with angular blocks of white or yellow pseudowavellite, and of banded wardite and millisite in variscite. Here again the minerals occurring with variscite in the core are later than the unfractured pseudowavellite shell, and in part later than the surrounding cavity; they must have replaced brecciated variscite selectively to retain the brecciated structure. It would be impossible for shearing stresses to have fractured the core without first crushing the outer shell. It is thus an antecedent breccia: the breccia was formed before the minerals that now comprise the breccia fragments.

The structural history then is simple: following the formation of the variscite nodules, minor to extreme brecciation occurred; the replacement of the variscite was in part guided by these fractures to produce pseudo-morphs after the original structures. No other fracturing or movement occurred.

(To be continued)

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