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Carminite and beudantite from the northern part of the Lake District and from Cornwall.

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Summary. The parageneses are given of ten new occurrences of carminite [$PbFe_2(AsO_4)_2(OH)_2$] and eleven of beudantite [$PbFe_3AsO_4SO_4(OH)_6$] in Cornwall and Cumberland, with an account of the alteration of carminite to beudantite and of beudantite to plumbojarosite or to beaverite.

CARMINITE and beudantite are both rare minerals for which very few localities have hitherto been recorded. Hingston Downs Consols mine,[1] Calstock, Cornwall, was for many years the only known British locality for carminite; more recently two further Cornish occurrences, at Wheal Gorland, Gwennap, and at Penberthy Croft mine, St. Hilary, have been recorded,[2] and it is probable that carminite is or has been present at other localities in the West of England. The first recorded British occurrence of beudantite was at Penberthy Croft mine,[3] since when one of us (A. W. G. K.) has found beudantite at some additional Cornish localities: Wheal Gorland; Wheal Carpenter, Gwinear; and Hingston Downs Consols mine. In his account of carminite from this latter mine, Russell mentioned that pharmacosiderite was an associated mineral but that beudantite was not present on his specimens; examination of some scorodite collected near Hitchen's shaft, on the South Lode, by one of us (A. W. G. K.) shortly after the discovery of beudantite at Penberthy Croft mine, has shown minute tufts of brick-red carminite needles accompanied by yellow to yellowish-brown beudantite.

During the last few years we have found that both carminite and

[1] A. Russell, Min. Mag., 1910, vol. 15, p. 255.

[2] A. W. G. Kingsbury, Trans. Roy. Geol. Soc. Cornwall, 1954, vol. 18, part 4 (for 1952), p. 395.

[3] Ibid., p. 392.

beudantite are relatively widespread in the northern part of the Lake District and we have confirmed eight new occurrences of carminite and ten of beudantite. Moreover, our field-work has furnished abundant evidence that carminite is somewhat unstable, and under certain conditions of oxidation or weathering is liable to alter into beudantite. This liability of carminite to alter may well account for its rarity, and for its having been found only in small amounts at nearly all the few recorded localities, except perhaps at Mapimi, Durango, Mexico. At many of these new occurrences, beudantite is unquestionably derived from the alteration of carminite; at others it appears to be of independent formation, but both types show that beudantite itself may undergo further alteration to plumbojarosite or to beaverite, which are closely related species but contain no arsenic.

Where distinctly crystallized, beudantite from Cornwall and Cumberland usually tends to have an acute rhombohedral habit, probably $\{11\bar{1}\}$, as opposed to the more 'cuboid' rhombohedral habit, $\{100\}$, such as is generally shown by the better-known Horhausen and Laurium crystals. This latter habit, which closely resembles that of pharmacosiderite, does, however, occur on some of the Penberthy Croft specimens and also on some specimens from two of the Cumberland localities; at one of the Cumberland localities an unusual hexagonal platy habit has also been found.

Alteration of carminite. It has become clear that much of what was originally carminite, both in Cornwall and in Cumberland, is now represented by pseudomorphs or replacement formations of beudantite; numerous specimens have been found showing this alteration actually in progress, where aggregates of carminite have changed to beudantite on the outside, but still contain an unaltered core of carminite. Since the occurrence of carminite at Wheal Gorland was described, one of us (A. W. G. K.) has collected further specimens at this locality, showing various habits of both carminite and beudantite; some of these, though small, illustrate the alteration in the clearest and most convincing way. In one instance crystalline and crystallized carminite, and yellowish beudantite, were found in a joint in the veinstone, together with green globules; some of the latter had broken across, revealing the radial-fibrous structure and an unaltered core of carminite surrounded by a zone of beudantite. This zone varies slightly in thickness in different globules, but the alteration is here clearly proceeding inwards from the surface; exactly similar radial-fibrous globular aggregates of greenish-brown beudantite have been found at Penberthy Croft mine, but in

most of these the change is almost complete and practically no trace of carminite remains. These aggregates are one of the characteristic habits of carminite. In two other examples, from Wheal Gorland, small acicular crystals of carminite were found to be in the process of altering to beudantite from one end. In many cases, however, the two minerals occur together with no signs of alteration, and appear to have been formed independently.

Alteration of beudantite. At a number of these new localities, particularly in Cumberland, we have found, in addition to well-defined beudantite, other closely similar minerals, which show departures from normal beudantite and which are in various stages of transition to plumbojarosite or beaverite or both. These alterations are clearly seen on many of the specimens, sometimes through the whole sequence

carminite $[PbFe_2(AsO_4)_2(OH)_2] \rightarrow$ beudantite $[PbFe_3AsO_4SO_4(OH)_6]$

$\rightarrow$ plumbojarosite $[PbFe_6(SO_4)_4(OH)_{12}]$

or

carminite $\rightarrow$ beudantite $\rightarrow$ beaverite $[Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6]$,

with the final elimination of AsO_4. In addition to, and often associated with, these alterations, we have also found well-defined beudantite, plumbojarosite, and beaverite, whose formation appears to have taken place independently; in general, these independent formations appear to have been derived from galena by direct alteration, or perhaps from cerussite, and are usually composed of dense, powdery aggregates without any evidence of derivation from carminite. Nevertheless, some of the plumbojarosite and beaverite and intermediate minerals are clearly the result of further alteration of beudantite.

In the alunite $[A'B'''_3(SO_4)_2(OH)_6]$ and beudantite $[A''B'''_3(As,P)O_4 SO_4(OH)_6]$ groups, both the A and B cation positions, and particularly the former, appear to be very tolerant as regards ionic size.[1] There may be a range of substitution in the A position as is shown, for example, between jarosite and natrojarosite, and a more limited substitution in the B position as is shown between alunite and jarosite; a considerable range of compositional variation is also shown by some members of the isostructural plumbogummite $[A''B'''_3((P,As)O_4)_2(OH)_5.H_2O]$ group. In the beudantite group, according to the limited amount of published data available, there is also some substitution among the anions (for example, of AsO_4 for PO_4 in corkite, the phosphate analogue of beudantite), while

[1] Dana, Syst. Min., 7th edn, vol. 2, p. 556.

some analyses of other phosphate members of the group show a departure from the 1:1 ratio between SO_4 and PO_4. The analysis and designation as 'beudantite–plumbojarosite', however, of the mineral from the Belvedere gold mine, Mount McGrath, Western Australia,[1] not only shows a gradation towards the jarosite group and a departure from the normal 1:1 ratio of AsO_4 to SO_4, with a decrease of AsO_4 and PbO and an increase of SO_4 and Fe_2O_3, but suggests that this particular mineral falls within the alteration-series mentioned above in connexion with the Cornish and Lake District occurrences. Very few occurrences of beudantite have so far been recorded; Dana[2] mentions the Mount McGrath occurrence and three others, and Guillemin[3] has recently recorded beudantite with carminite from Cap Garonne, Var, France. This paucity of recorded occurrences would account for the lack of data on variations in the cation and particularly the anion ratios. With the exception of the Western Australian occurrence, and those in Cornwall and the Lake District, the presence of beudantite does not appear to have been recorded with any of the other numerous occurrences of plumbojarosite and beaverite, so that the alteration-sequences referred to above have not been observed.

It may be that local oxidation conditions in the veins in Cornwall and in the Lake District, largely as the result of their mineral assemblages, gave rise to these particular alterations. In this connexion it is to be noted that in all these Cornish and Lake District occurrences, arsenopyrite is present in the veins as well as other-sulphides of iron, copper, lead, and zinc.

Because of the small amount of available material, often closely associated with other minerals, identification has been carried out mainly by X-ray study. Using cameras of 9-cm., 11·46-cm., and 19-cm. diameter, powder-photographs of a large number of samples have enabled specimens of beudantite, plumbojarosite, and beaverite to be distinguished clearly, not only from each other but from other minerals in the alteration series. Almost pure beudantite crystals from Laurium in Greece have furnished our standard photographs of this mineral. Samples of analysed plumbojarosite from the Tintic Standard mine, Utah, and from other well-known American localities, have been generously supplied by Dr. W. T. Schaller, of the U.S. Geological Survey, and also by Professor Horace Winchell, from the Brush Collection at the

[1] E. S. Simpson, Journ. Roy. Soc. Western Australia, 1938, vol. 240, p. 110.
[2] Syst. Min., 7th edn, vol. 2, p. 1002.
[3] Bull. Soc. Franç. Min. Crist., 1952, vol. 75, p. 70 [M.A. **12**–68].

University of Yale; Dr. Schaller also supplied a sample of beaverite from his analysed type-material,[1] and we thank him and Professor Winchell for their help and generosity. From the large number of powder-photographs obtained it has been possible to see if and where specimens of the various Lake District and Cornish minerals were intermediate between beudantite and plumbojarosite or beaverite; in a number of cases it was evident that the specimens were mixtures. Among the intermediate minerals many of the patterns and spacings showed the characteristics of both beudantite and one of the other two species (indicating a probable half-way alteration); others again showed probable compositional variations or almost complete alteration. While chemical analyses in conjunction with the X-ray studies would obviously have been desirable, had they been practicable, the results obtained have nevertheless indicated clearly the processes that appear to have been taking place.

New occurrences of carminite and beudantite. As carminite and beudantite, as well as other minerals in the alteration series referred to above, occur together at many of the new localities found, both in the Lake District and in Cornwall, it is convenient to list them under the localities with a description of their associations.[2]

Lake District, Cumberland.

Grains Gill, Carrock Fell. Beudantite has been found here as brown, powdery aggregates in gossany material from near the intersection of an east–west 'lead-vein' with the north–south Emerson vein of the 'granitic' suite. Associated minerals fall within the alteration series referred to above, but carminite appears to be absent from this locality.

Higher part of Brandy Gill, Carrock Fell. About three-quarters of the way up the gill, an east–west Cu–Pb–As vein, in altered granophyre, outcrops on the west side. This vein intersects, and in each case displaces to the left, a number of north–south veins and strings, which form the northern extremities of the more westerly members of the 'granitic' suite of veins in Grains Gill[3] half a mile to the south. These 'granitic' veins and strings in the higher part of Brandy Gill, as well as the adjacent country-rock, contain much arsenopyrite; oxidation of this, or reaction

[1] Butler and Schaller, Journ. Wash. Ac. Sci., 1911, vol. 1, p. 26; Amer. Journ. Sci., 1911, ser. 4, vol. 32, p. 418.

[2] See also A. W. G. Kingsbury and J. Hartley, Min. Mag., 1956, vol. 31, p. 289, and 1957, vol. 31, p. 700.

[3] In Grains Gill several east–west 'lead-veins' also heave and shift to the left the main 'granite' veins; later quartz–carbonate veins cross and heave them to the right.

with the mineralizing solutions and minerals of the east–west vein, has produced a great variety of secondary arsenates. Carminite must formerly have been abundant and, though not rare, most of it has now altered to beudantite. Small unaltered patches of carminite are fairly widely distributed through and on the altered granophyre walls of the vein; on the cheeks of the vein it is associated with large amounts of beudantite, which forms crystalline coatings and crusts, yellow, yellow-green, greenish-brown, and brown in colour, most of which are pseudomorphous after or derived from alteration of carminite. In one instance a hollow hexagonal epimorph was found (probably after mimetite) of which one end consisted of carminite, the middle portion of beudantite, and the other end of beaverite. At the intersections with the east–west vein, which were examined *in situ*, the north–south strings are themselves impregnated with carminite for several inches on either side of the east–west vein. Most of the carminite shows the characteristic deep carmine-red colour, and usually forms drusy botryoidal or crystalline aggregates and crusts: it has also been found in cavities in the vein, where it is usually associated with beaverite (some of which has formed directly from and is pseudomorphous after galena), mimetite, and bayldonite, and occasionally it occurs in minute prismatic crystals.

In addition to its widespread occurrence in the wall-rock, beudantite has been found well crystallized in quartz in the vein, both as aggregates of small brown acute rhombohedra, and as small (up to 2 mm.), brown, partly zoned hexagonal plates: the latter show a large basal plane and narrow faces of two rhombohedra or of the hexagonal prism or of all three, and this appears to be the first recorded occurrence of this euhedral platy habit. A little carminite is associated with beudantite of both habits.

Dry Gill mine, Caldbeck Fells. Beudantite has been found here, in material from the middle cross-cut about half-way up the gill, as greenish-yellow powdery aggregates associated with olivenite, and in material from the lower day-level[1] as yellow crystalline and brown fine-grained aggregates, with baryte, azurite, and 'psilomelane'. Some of this material appears to be derived from carminite, although no traces of the latter have yet been found.

Driggith mine, Caldbeck Fells. Carminite occurs in very small patches, associated with yellowish-brown microcrystalline beudantite, mimetite, and cerussite, an iron-stained granular quartz from the outcrop of the main vein. Beudantite also occurs in yellow-brown to brown powdery

[1] Driven alongside the vein where it outcrops and crosses the Dry Gill beck.

aggregates investing decomposing galena and cerussite from the outcrop of the vein; some of this beudantite falls within the alteration-series mentioned above (p. 425).

Netherrow Brow, Caldbeck. (*a*) In iron-stained spongy quartz vein-stone derived from an old cross-cut between Sandbed mine and Pottsgill barytes mine, driven to the near-outcrop of a north-west–south-east vein, carminite occurs as small residual patches with considerable amounts of yellow-green, yellow-brown, and brown earthy and micro-crystalline beudantite, together with red-brown scorodite, beaverite, and 'limonitic' matter. (*b*) In material from an old level, near the farm of Nether Row, driven on the same vein as the preceding and about 800 yards to the north-west, carminite occurs in small drusy globular aggregates, associated with small yellow acute rhombohedra of beudantite, brown scorodite, and minute tufts of arseniosiderite. Beudantite also occurs in considerable amounts as compact yellow, yellow-brown, green-brown, and brown powdery and micro-crystalline aggregates associated with yellow mimetite, mottramite, green and brown scorodite, pharmacosiderite, and yellowish and yellowish-brown powdery plumbojarosite and beaverite. A few 'cuboid' rhombohedra of beudantite have been found on some specimens. The unaltered vein material carries fine-grained and disseminated arsenopyrite, pyrite, galena, some blende, and traces of chalcopyrite.

Pottsgill barytes mine, Caldbeck. At the head of the Gill Beck a small copper vein, apparently north-north-west–south-south-east, was cut by the old No. 1 cross-cut of the barytes mine and much material from it lies on a small dump near the entrance to the cross-cut. The vein apparently contained mainly chalcopyrite, together with galena, blende, and arsenopyrite or other arsenic-bearing minerals. There are also in the vicinity a number of small veins and strings carrying galena, pyrite, arsenopyrite, and some löllingite, some of which may also have been cut by the cross-cut. Among the material derived from the copper-vein, carminite has been found in tufts of minute, brick-red, tapering acicular crystals associated with acute rhombohedra of yellow-brown beudantite, scorodite, and pharmacosiderite, in a gossany quartz–goethite matrix. Beudantite also occurs as a powdery yellow to yellow-brown coating on altering galena.

Ingray Gill, Caldbeck (*between Haygill and the hamlet of Fellside*). An unrecorded north-north-west vein crosses the head of the gill and has two cross-cuts on it; the whole area is covered with drift, and no signs of the vein outcrop are visible. In material from the northern cross-cut, a little

carminite is present as tufts of minute prisms in cavities in saccharoidal quartz, associated with beudantite in minute yellow rhombohedra, scorodite, and pharmacosiderite. Beudantite is also present, forming yellowish-brown powdery and crystalline coatings on decomposing galena and quartz.

Higher Roughton Gill, Caldbeck Fells. Carminite has been found in the outcrop of the main south vein, along the south-eastern flank of Balliway Rigg, forming drusy botryoidal aggregates and tufts of minute prisms in cavities in quartz, with yellow rhombohedra of beudantite, some of them attached to the surface of the carminite, and small, colourless, tapering prisms of mimetite. Beudantite has also been found here as yellowish-brown, greenish-brown, and brown powdery and crystalline aggregates associated with decomposing galena, cerussite, chrysocolla, jarosite, and plumbojarosite, and minerals in the alteration-series beudantite to plumbojarosite and beudantite to beaverite.

Wanthwaite mine, St. John-in-the-Vale, near Threlkeld. Two veins were worked at this little-known mine: (*a*) The southern vein, occupying the faulted junction between Skiddaw Slates and the Borrowdale Volcanic Series, under Wanthwaite Crags, is mainly a fault-breccia of smashed slate cemented by quartz, carbonates, and various sulphides; it also contains, on the hanging-wall, a thick rib of quartz impregnated with a massive granular intergrowth of arsenopyrite, pyrite, galena, blende, and, rarely, traces of chalcopyrite. At the outcrop, *in situ* on the hanging-wall, this rib has oxidized to iron-stained skeletal quartz, cavities in which now contain small residual patches of carminite, with large amounts of yellow, yellowish-green, buff, and brown beudantite, some of it powdery and some minutely crystallized, with scorodite, both green and reddish-brown, and pharmacosiderite. Traces of 'cuboid' rhombohedra of beudantite, largely altered, also occur here. (*b*) The northern vein, in the (probably) faulted boundary between the Skiddaw Slates and the Threlkeld microgranite, on Wanthwaite Bank and up to Clough Head, contains similar primary minerals but in smaller amounts. Yellow-brown beudantite, part powdery and part micro-crystalline, occurs together with minerals in the beudantite → plumbojarosite alteration-series on decomposing galena from a lower level on the vein on Wanthwaite Bank.

New localities for beudantite in Cornwall.

Wheal Gorland, Gwennap. Beudantite here occurs as minute, yellow rhombohedra on the surface of drusy botryoidal carminite; also as yellow,

yellowish-green, and green drusy crystalline crusts, and green globular aggregates, associated with and partly pseudomorphous after carminite, in joints in a pink quartz matrix; it is also closely associated with zeunerite[1] and mimetite.

Wheal Carpenter, Gwinear. Beudantite here occurs as yellowish-green to greenish-brown crystalline crusts associated with bayldonite, on quartz. Small amounts of carminite also occur, in such a manner as to suggest that the beudantite has formed at its expense.

Specimens collected more recently at Penberthy Croft mine, St. Hilary, show beudantite in crusts, globular aggregates after carminite, and 'cuboid' rhombohedra, with a remarkable range of colour through various shades of yellow, green, and brown to almost black; some of these specimens also show small residual patches of carminite. Further examples of intermediate beudantite → beaverite and beudantite → plumbojarosite have also been found.

Although the carminite from all these localities, both in the Lake District and in Cornwall, has a characteristic appearance and is in most cases readily recognizable in the field, all the occurrences have been verified by X-ray and other methods, and powder-photographs have all shown agreement with those of carminite from Mapimi and from previously confirmed Cornish occurrences.[2]

Note: Since this paper was originally prepared, one of us (A. W. G. K.) has found three more localities in Cornwall for carminite and beudantite:

Treore mine, St. Teath. This locality lies immediately south of Treore farm, about $1\frac{3}{4}$ miles east-south-east of Port Isaac. The vein, trending north-north-east, was at one time worked for arsenic, being rich in arsenopyrite and pyrite in a gangue of brecciated slate and quartz, chalybite, and ankeritic carbonates. Associated ore minerals are galena, chalcopyrite, blende, stibnite, jamesonite, and other antimony-bearing sulphides. The principal secondary minerals are mimetite and scorodite, carminite and beudantite occurring in association with these. One specimen is of particular interest in that it shows two alteration-sequences:

[1] A. W. G. Kingsbury, Trans. Roy. Geol. Soc. Cornwall, vol. 18, part 4 (1952), p. 396. A sample of this material, examined shortly after collection, was shown to be zeunerite, with n 1·608 ± 0·001 and giving X-ray powder-pattern spacings almost identical with those for synthetic hydrous zeunerite given by J. Weiss-Frondel in Amer. Min., 1951, vol. 36, p. 252, and distinct from those of meta-zeunerite with 5–8 H_2O.

[2] Representative specimens of most of the above occurrences have been given to the Department of Mineralogy, British Museum (Natural History).

in one, crystals of mimetite have been partially or completely replaced by pseudomorphs of carminite, which in turn has partially or completely altered to beudantite; in the other sequence, larger areas of green beudantite are accompanied by patches of residual carminite, some of which are coated with yellow rhombohedra of beudantite of later formation, and some patches of the green beudantite are sprinkled with a second generation of mimetite crystals.

Old Treburgett mine, St. Teath. This mine lies about $2\frac{1}{4}$ miles east by south of Treore mine, and $\frac{3}{4}$ mile south-west of St. Teath village, on the northern part of a north-east vein and an associated cross-course. A gangue of brecciated country-rock and quartz, with calcite, ankerite, and chalybite, carried galena and blende as the principal ore minerals, with minor arsenopyrite and some antimony-bearing sulphides. Carminite occurs in cavities in decomposing arsenopyrite as drusy botryoidal aggregates, together with a little yellow beudantite, scorodite, and traces of mimetite. Very little alteration of the carminite has taken place at this locality.

Pengenna (Trewethen) mine, St. Kew. This locality lies about $\frac{3}{4}$ mile south-west of Old Treburgett mine, on the southern part of the same vein (here known as the Trewethen lode) and on another vein (the Pengenna lode) trending nearly due north. The latter vein carried some antimony minerals in the upper part, but mainly galena in depth. Both carminite and yellowish beudantite are present in the oxidized vein-material, associated with mimetite and scorodite.