

PHOSPHATE MINERALS IN THE CASTLE DOME COPPER DEPOSIT, ARIZONA

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ABSTRACT

Several phosphate minerals occur in the Castle Dome copper deposit near Miami, Arizona, some of which are of special interest because of their uncommon occurrence in deposits of this type. They comprise apatite, turquoise, wavellite, metatorbernite, and libethenite. Apatite is a primary constituent of the quartz monzonite host rock. Turquoise and libethenite are probably supergene minerals, whereas wavellite and metatorbernite may possibly have been introduced by late hydrothermal solutions.

INTRODUCTION

The Castle Dome copper deposit is in the Globe-Miami mining district, Gila County, Arizona, five miles west of Miami. The Castle Dome open-pit mine, on the south slope of Porphyry Mountain, is owned and operated by the Castle Dome Copper Company, Inc. It was developed by the owners as a war project, and since June 1943 has produced about 4,000,000 pounds of copper per month.

A detailed study of the Castle Dome deposit and the surrounding area was undertaken by the U. S. Geological Survey in 1943. A complete description will be published by the Survey at a later date.

The writer is indebted to Jewell J. Glass for her work on the properties of the libethenite and for checking the identification of the other minerals described. He wishes also to thank the Castle Dome Copper Company for permission to publish this paper.

THE COPPER DEPOSIT

The copper deposit is of the disseminated or "porphyry" type. The host rock is a body of quartz monzonite intruded into pre-Cambrian schists and quartzites and possibly into the lower part of the overlying Paleozoic strata. The quartz monzonite is much older than the copper mineralization which is probably genetically related to the Schultze granite south of the deposit. The Schultze granite is of probable late Cretaceous or early Tertiary age.

The most important hypogene sulfides in order of abundance are pyrite, chalcopyrite, and molybdenite. They occur in, or associated with, a set of narrow, closely spaced, generally parallel, quartz veins striking east-northeast and dipping steeply southward. The only other hypogene

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sulfides, sphalerite and galena, are present in relatively small amounts. They occur accompanied by some quartz, pyrite, and chalcopyrite in veins deposited along faults and major fractures many of which cut across the pyrite, chalcopyrite, and molybdenite veins. The sphalerite-galena veins are banded as if they had been deposited in open fractures, and commonly the vein minerals do not completely fill the fractures. They apparently represent a slightly younger phase of mineralization than the pyrite, chalcopyrite, and molybdenite veins. Small amounts of barite and fluorite, deposited on the walls of open fractures, were also late hypogene minerals.

The mineralizing solutions altered the quartz monzonite bordering the veins to quartz and sericite and caused general argillic alteration of the plagioclase throughout the mineralized area.¹

Although the ore body is partly the result of higher than average grade copper metallization associated with several gently dipping diabase sills intruded into the quartz monzonite, supergene enrichment played an important role in the formation of the ore. In the upper part of the ore body, chalcopyrite is partly replaced by chalcocite; but the enrichment has not progressed so far that pyrite is replaced except to a very minor extent in a few places. A little covellite is present throughout the the chalcocite zone, but it is generally abundant near the top where it formed by oxidation of chalcocite. Oxidized copper minerals, including malachite, azurite, cuprite, and native copper, occur sparsely throughout the leached and chalcocite zones. Turquoise is also fairly common in these zones.

PHOSPHATE MINERALS

In addition to the common sulfides and supergene minerals, a number of phosphates occur in the deposit, some of which are of special interest because of their uncommon occurrence in this type of ore body. They comprise apatite, turquoise, wavellite, metatorbernite, and libethenite. Apatite and turquoise are widely distributed; whereas wavellite, metatorbernite, and libethenite are present only in certain parts of the mine.

Apatite.—Apatite is an accessory constituent of the quartz monzonite host rock in which it occurs associated with biotite in a manner common in rocks of this kind. No apatite introduced by hydrothermal solutions has been recognized. It is mentioned here as a possible source of the phosphate ion in the other minerals.

The phosphate content of the fresh and hydrothermally altered quartz monzonite, as determined by chemical analysis, is shown as follows:

¹ Peterson, N. P., Gilbert, C. M., and Quick, G. L., Hydrothermal alteration in the Castle Dome copper deposit, Arizona: *Econ. Geol.*, **41**, 820-840 (1946).

Sample No	1	2	3	4	5
P ₂ O ₅	.23	.19	.13	.13	.08%

Samples 1 and 2. Unaltered quartz monzonite
 Sample 3. Altered quartz monzonite (clay phase)
 Sample 4. Altered quartz monzonite (clay-sericite phase)
 Sample 5. Altered quartz monzonite (quartz-sericite phase)

Apatite is the only phosphate mineral that was recognized in thin sections of the analyzed rocks. On the basis of these analyses, the fresh rock contains about 0.5 per cent apatite. From 40 to 60 per cent of it is destroyed by hydrothermal alteration. Apatite is generally considered to be a fairly stable mineral but is soluble in acids and is undoubtedly dissolved by supergene solutions to some extent. It could therefore serve as a source of phosphate ion in the formation of supergene minerals.

Wavellite, $3Al_2O_3 \cdot 2P_2O_5 \cdot 13(H_2O, HF)$.—Wavellite is restricted largely to a relatively small elongate area, which trends parallel to the mineralized veins, in the central part of the ore body. It appears to be localized along fractures dipping moderately north to northwestward, which cut the steeply southward dipping veins at approximately right angles. Where open spaces occur along the fractures, wavellite forms encrustations on the walls and on earlier minerals deposited on the walls of the fractures. The crusts consist of coalescing hemispherical masses up to 4 mm. in diameter with radiating internal structure. The surfaces of the hemispheres glisten with light reflected from countless crystal faces. Some of the crusts are clear and colorless, others are gray, yellow or pale-green. In the weathered zone the crusts are usually translucent white or may be stained by iron.

Metatorbernite, $CuO \cdot UO_3 \cdot P_2O_5 \cdot 8H_2O$.—Metatorbernite was first recognized as an artificial mineral by Hallimond.² He obtained it by dehydration of torbernite. The first inversion of torbernite in contact with water occurs at 75° C. It is accompanied by a marked change in optical properties and a loss of four molecules of water. A second inversion takes place at 130° C. with further loss of water. The two products were designated by Hallimond as metatorbernite I and II, respectively. He was unable to bring about a reversal of the transformations. Metatorbernite I was later recognized as a natural mineral from Spain and Cornwall by N. L. Bowen.

² Hallimond, A. F., The crystallography and dehydration of torbernite: *Mineral. Mag.*, 17, 326-339 (1916).

The metatorbernite in the Castle Dome deposit was, almost without exception, deposited on wavellite crusts. It occurs as very thin, rectangular, bright-green plates which are usually arranged in tiny rosettes of extraordinary beauty. In some places the crystals form a moss-like mat covering the wavellite crusts. Examined in immersion oils, the crystals are seen to be rectangular or to show rectangular cleavage. Plates lying face up show no birefringence and have an index of refraction of 1.623. The other index is slightly higher. Tilted plates show anomalous purple to violet interference colors and slight pleochroism from yellowish-green to greenish-blue. These properties identify the mineral as metatorbernite I described by Hallimond.³ Bowen⁴ studied the abnormal birefringence of metatorbernite I and found the mineral to be positive for the red end of the spectrum, negative for the blue end, and isotropic in green light at about 515 μ .

The metatorbernite in the Castle Dome deposit is present only in very small amounts.

Libethenite, $4\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$.—Libethenite has been found only along fractures related to the Dome fault system which is the most prominent structural feature in the mine and consists of several normal faults trending northeastward through the central part of the ore body. Like wavellite and metatorbernite, it occurs only in open fractures where it forms crusts which are generally composed of tufts of small, emerald-green prisms or a drusy mat of acicular crystals. In some places discrete crystals, some so small they cannot be recognized without the aid of a lens, others up to 1.5 mm. long, lie flat on the rock surfaces.

Jewell Glass of the Geological Survey studied several specimens of the mineral and described its physical and optical properties as follows:

Crystals are usually short prisms two to five times as long as they are thick, passing into acicular forms grouped in radiating clusters, united in druses. A few crystals show pyramidal habit, resembling octahedrons. Cleavage is good prismatic, luster vitreous, color emerald to yellowish-green, transparent.

Optically the mineral is biaxial negative, $2V$ large, about 85° . An optic axis emerges normal to a prismatic cleavage or a side pinacoid and looks like the familiar optic axis on epidote grains. The plane of the optic axis is across the elongation. Twinning is observed occasionally. Dispersion is strong, $r > v$. The fragments are pale-green, pleochroism faint, seldom distinguishable. Extinction inclined 0° to 20° , greater than 20° in a few grains. Indices of refraction, average of several readings on each specimen, are: $\alpha = 1.703$, $\beta = 1.746$, $\gamma = 1.789$; $B = 0.086$, all ± 0.002 .

³ Hallimond, A. F., Metatorbernite I, its physical properties and relation to torbernite: *Mineral. Mag.*, **19**, 43-47 (1920).

⁴ Bowen, N. L., Abnormal birefringence of torbernite: *Am. Jour. Sci.*, 4th ser., **48**, 195-198 (1919).

The explanation for the anomalous inclined extinction of the libethenite may be revealed by its x -ray diffraction pattern which has not as yet been studied.

Wulfenite, $PbO \cdot MoO_3$.—Wulfenite, although not a phosphate, is discussed here because of its close association with libethenite. It was identified on fragments of rock broken by blasting and has not been seen in place. Instead of the usual tabular crystals, the Castle Dome wulfenite occurs as small, pointed, tetragonal prisms, rarely over 3 mm. long and generally much smaller, which are attached to fragments of rock that apparently formed the walls of open fractures. The surfaces of the rock, as well as some of the crystals, are coated with limonite, jarosite, canbyite, and malachite, all of undoubted supergene origin.

Turquoise, $CuO \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 9H_2O$.—Turquoise is fairly widespread throughout the chalcocite zone and in the leached capping. A hard variety of gem quality occurs in small veinlets up to one-quarter inch thick and also in concretion-like masses up to one-half inch thick and several inches across. Its color ranges from sky-blue to bluish-green, the blue variety predominating. It is generally associated with clay minerals and sericite which form selvages on the veins and masses and are commonly included in the turquoise. Seen under the microscope, it is a microcrystalline aggregate having a mean index of refraction of 1.62.

Much more abundant than the hard blue turquoise is a soft chalky variety which occurs in small masses on the walls of open fractures or filling small fractures. The masses and seams were not formed by alteration or replacement of wall-rock but appear to be accumulations of material transported into the fractures either in solution or in suspension in ground water. Its color ranges from almost white to light-blue when dry and deeper shades of blue when moist. The powdered mineral in immersion oils is almost identical in appearance to the powdered hard variety and has the same index of refraction. When ignited, the powder turns brown, becomes soluble in acid and gives positive reactions for copper and phosphate ions. All gradations between the hard blue turquoise and the white chalky variety can be found.

A few specimens of a light-green, iron-bearing copper aluminum phosphate were found occurring in the same manner as the hard blue turquoise. It is a microcrystalline aggregate whose mean index of refraction is 1.67. Charles Milton of the Geological Survey identified the mineral as a ferrian turquoise. He reports as follows:

The light-green mineral is identified as turquoise rather than chalcosiderite. These two minerals are considered to be isomorphous with Al_2O_3 and Fe_2O_3 , respectively. The x -ray pattern is similar to that of turquoise from Lynch, Va., which presumably

would hardly be distinguishable from chalcosiderite. However, the density (2.75 by pycnometer) and indices of refraction indicate turquoise.

Employees of the mine have been permitted to dig turquoise on days when they were not on duty, and an amazingly large quantity of the mineral has been purchased by dealers in Globe and Miami. Unfortunately no record is available as to the amount of turquoise produced, but undoubtedly the Castle Dome mine is one of the most important sources of gem turquoise at the present time.

ORIGIN OF THE PHOSPHATES

Although some of the Castle Dome phosphates were probably formed by supergene processes, the lack of valid evidence of supergene origin in the case of wavellite and metatorbernite suggests that they were deposited by hypogene solutions which may represent either the final ebbing stages of the copper mineralization or an entirely different period of mineralization from an independent source. No minerals have been recognized in the deposit from which uranium could have been derived by weathering processes. If it had been leached from undetectable traces present in the country rock, the metatorbernite would be expected to have more general distribution instead of being concentrated in a relatively small portion of the mineralized area. The absence of an obvious source of uranium is probably not conclusive evidence that metatorbernite was deposited by hypogene solutions, however, no evidence has as yet been found that suggests supergene origin.

Metatorbernite is less widely distributed than wavellite which commonly occurs alone; however, metatorbernite is never found unaccompanied by wavellite. It usually occurs on wavellite crusts and is clearly the younger mineral. Metatorbernite has not been recognized in the leached capping. Most of it has been found in the lower part of the secondary sulfide zone; the maximum depth at which it occurs cannot as yet be determined. In a few places, metatorbernite has been dissolved by supergene solutions leaving a very little residue of a yellowish material resembling kaolinite.

The fact that torbernite transforms to metatorbernite I at 75° C. and to metatorbernite II at 130° C. may indicate that metatorbernite I formed at a temperature between 75° and 130° C. which is certainly above the range of supergene solutions; however, it has not been produced artificially except by dehydration of torbernite, hence there is as yet no proof that metatorbernite I cannot be precipitated from solution at temperatures lower than 75° C.

Jewell Glass⁵ describes an instance in which the inversion of torbernite

⁵ Glass, Jewell J., personal communication.

to metatorbernite I unquestionably took place at room temperature. A specimen of torbernite from Spruce Pine, N. C., stored in a mineral cabinet in the Geological Survey laboratory was reexamined after a lapse of about ten years and was found to have inverted to metatorbernite I. The time required for the inversion to take place at room temperature is not known since no interim examination of the specimen was made; however, it was observed that after a few months, or perhaps years, the emerald-green color of the torbernite had faded to a dull siskin green, and the crystals had lost their transparency.

Very little wavellite has been found in the weathered zone. In a few places in the upper part of the ore body, the wavellite shows evidence of attack by supergene solutions; and some of it is stained by iron oxides; however, much of it occurs in fractures where chalcopyrite is only slightly tarnished by chalcocite and where no other supergene minerals are present. Wavellite commonly crusts pyrite and chalcopyrite, and in one place it was deposited on fresh galena and sphalerite. Many examples of wavellite crusts on barite crystals have been observed.

Wavellite probably forms as a supergene mineral in the weathering of phosphate deposits, but where it occurs in vein deposits it is most likely hypogene, although opinions differ on this point. Lindgren and Ransome⁶ describe hypogene wavellite associated with adularia in the Cripple Creek district. Russell⁷ describes wavellite in the Castle-an-Dinas wolfram mine in Cornwall so as to suggest to the reader that it is a late hydrothermal mineral. The wavellite in the tin veins of Llallagua, Bolivia, is considered hypogene by Turneure⁸ and Bandy,⁹ but Samoyloff¹⁰ and Ahlfeld¹¹ include it among the supergene minerals. In a later discussion of the same tin deposit, Ahlfeld¹² describes wavellite as one of the latest hypogene minerals.

Libethenite crystals are always present on those surfaces of rock fragments to which wulfenite crystals are attached, but many specimens contain libethenite crystals unaccompanied by wulfenite. Both minerals occur in fractured rocks where oxidation and leaching of sulfides are probably complete. The fractures contain abundant limonite, canbyite, malachite, and jarosite. These minerals are clearly younger than the

⁶ Lindgren, W., and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: *U. S. Geol. Survey, Prof. Paper* 54, 176 (1906).

⁷ Russell, Arthur, quoted, Russellite, a new British mineral: *Mineral. Mag.*, 25, 41 (1938).

⁸ Turneure, F. S., The tin deposits of Llallagua, Bolivia: *Econ. Geol.*, 30, 60 (1935).

⁹ Bandy, M. C., Direction of flow of mineralizing solutions: *Econ. Geol.*, 37, 330 (1942).

¹⁰ Samoyloff, V., The Llallagua-Uncia tin deposit: *Econ. Geol.*, 29, 495 (1934).

¹¹ Ahlfeld, F., The tin ores of Uncia-Llallagua, Bolivia: *Econ. Geol.*, 26, 253 (1931).

¹² Ahlfeld, F., The tin deposits of Llallagua, Bolivia: *Econ. Geol.*, 31, 220 (1936).

wulfenite, but their relationship to libethenite is not clear. In some places libethenite crystals are engulfed by them, in other places libethenite crystals appear to have formed on limonite crusts. Clumps of libethenite crystals are commonly attached to wulfenite in such a manner as to suggest that libethenite is decidedly the younger mineral. Thin botryoidal crusts of a black manganiferous mineral resembling pyrolusite are often found on the same rock surfaces with libethenite, which in some examples forms crusts on the manganese mineral. No other occurrence of manganese oxides has been noted in the Castle Dome deposit, hence it is considered to be related to this phase of mineralization. On some rock fragments, barite crystals are attached to the same surfaces as are wulfenite and libethenite, and both minerals appear to have formed on barite crystals.

Although wulfenite and some of the libethenite is clearly older than such definitely supergene minerals as limonite, malachite, canbyite, and jarosite, little evidence can be cited to support a postulation that they were deposited by late hypogene solutions. The usual difficulty in accounting for a source of molybdenum to produce wulfenite by supergene processes is solved in this deposit by the presence of molybdenite, which, although very resistant to oxidation, has been altered to the oxide to some extent; and therefore some molybdenum may have been transported by supergene solutions. Likewise a source of lead is available in galena which is more abundant along the Dome fault system than elsewhere in the deposit. However, Dittler's¹³ experiments on the synthetic production of wulfenite indicate that an alkalic environment is necessary, and therefore wulfenite is not likely to be formed by supergene solutions. He concludes that it is formed by rising alkaline solutions which reacted with lead carbonate.

Sources of the constituents of libethenite are also readily available in this deposit. The copper could have been derived from hypogene chalcocopyrite, and phosphate ion from apatite or wavellite. Lindgren¹⁴ found small crystals of libethenite in cavities and seams in quartzite in the oxidized zone of the Coronado vein in the Clifton-Morenci district. He considered it to be a supergene mineral.

On the basis of field evidence, wulfenite and libethenite are clearly late minerals and may well be of supergene origin; however, wulfenite is earlier than libethenite, and the two minerals are not necessarily genetically related. Their association could easily be coincidental.

¹³ Dittler, E., Further experiments on the synthetic production of wulfenite: *Zeits. Kryst. Min.*, **54**, 332-342 (1914).

¹⁴ Lindgren, W., Copper deposits of the Clifton-Morenci district, Arizona: *U. S. Geol. Survey, Prof. Paper* **43**, 118 (1905).

Turquoise is generally conceded to be a supergene mineral, formed by the action of ground-water solutions, carrying copper and phosphate ions, on kaolin and possibly sericite. Various writers describe all stages in the alteration from copper-stained kaolin to hard blue turquoise; but it is not usually clear from the published descriptions whether the mineral is kaolinite or some other clay. Kaolinite is not a common mineral in the Castle Dome deposit, and its association with turquoise has not been noted; however, turquoise is commonly associated with beidellite, halloysite, and sericite. No evidence has yet been found suggesting that it forms from clay. The hard blue turquoise grades into the soft, white clay-like variety; but the index of refraction of all of it is near 1.62, which is much higher than that of any of the clays present. None of the material could be construed as being transitional between turquoise and the associated clays.

Although turquoise is most abundant in the upper part of the secondary sulfide zone, it is commonly found in deep fractures where chalcopyrite is only slightly replaced by chalcocite or not at all. If turquoise was formed by supergene solutions, the phosphate ion would have to be derived from either wavellite or apatite which are the only earlier phosphate minerals. Wavellite is apparently dissolved by supergene solutions, but much turquoise occurs in parts of the mine where no wavellite has been recognized. In the Castle-an-Dinas mine in Cornwall,¹⁵ wavellite spheres are commonly covered by minute botryoidal aggregates of bright-green turquoise, but no such association has been seen in the Castle Dome deposit. Most writers look to apatite as the probable source of phosphate ion even though admitting in some cases that the country rock contains very little apatite.

¹⁵ Hey, M. H., and Bannister, F. A., Russellite, a new British mineral: *Mineral. Mag.*, 25, 41 (1938).