

## Andrewsite and laubmannite formally discredited

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### ABSTRACT

Type andrewsite is formally discredited as a mineral species. The original material is a mixture of hentschelite and rockbridgeite, with minor chalcocyanite. Type laubmannite is also formally discredited as a mineral species. Fresh material is a variable mixture of dufrenite, kidwellite, and beraunite. Altered material is a mixture of dufrenite and much kidwellite with sparse beraunite. Both discreditations have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

### ANDREWSITE

#### Introduction

Andrewsite was first described by Maskelyne (1871, 1875) as a new mineral from the West Phoenix mine, near Liskeard, Cornwall, England (see also Foster, 1875; Collins, 1876; Kingsbury, 1952, 1957). Subsequent studies, however, have led to much confusion about the nature of this material and its putative relationship to laubmannite. The present report resolves the confusion in the literature and relieves the mineralogical nomenclature of two unnecessary names.

Frondel (1949) reported some additional data for purported andrewsite (X-ray and optical data), but the specimens studied by him are here shown to be dufrenite, which also occurs at the West Phoenix mine.

Maskelyne's type andrewsite was restudied in part by Claringbull and Hey (1958), who provided a new chemical analysis and unit-cell parameters. The analysis of Claringbull and Hey (1958) yielded CuO 16.9, FeO 7.7, Fe<sub>2</sub>O<sub>3</sub> 37.0, P<sub>2</sub>O<sub>5</sub> 32.4, H<sub>2</sub>O 6.8, total = 100.8 wt%, from which they derived the formula 4[(Cu,Fe)Fe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>], wherein Cu/Fe = 2/1. However, this formula is incorrect as presented; it does not agree well with either their analysis or the weight percentages that Claringbull and Hey indicated were calculated from this formula.

Moore (1970) suggested a relationship between andrewsite and rockbridgeite, using the unit-cell parameters of Claringbull and Hey (1958). Claringbull and Hey had reported a density of 3.50 g/cm<sup>3</sup>, unit-cell parameters  $a = 14.16$ ,  $b = 16.83$ ,  $c = 5.18$  Å, and space group *B22<sub>2</sub>*. Calculation of full unit-cell contents from the analysis of Claringbull and Hey (1958) yields Cu<sub>5.53</sub>Fe<sub>2.79</sub><sup>2+</sup>Fe<sub>12.06</sub><sup>3+</sup>P<sub>11.88</sub>H<sub>19.64</sub>O<sub>65.93</sub>. This yields a (Cu + Fe<sup>2+</sup> + Fe<sup>3+</sup>)/P/H ratio of nearly 5/3/5. This value is in good agreement with their calculated theoretical values and with the cation ratio in the structure of rockbridgeite. A recalculation of their analysis, on the basis of 17 O atoms, yields Cu<sub>1.43</sub>Fe<sub>0.72</sub><sup>2+</sup>Fe<sub>3.11</sub><sup>3+</sup>P<sub>3.06</sub>H<sub>5.06</sub>O<sub>17</sub>, which is in reasonable agreement with the composition of a hypothetical Cu analogue of rockbridgeite. However, as shown below, this is

misleading, and andrewsite has no relationship to rockbridgeite. The above computational results are merely fortuitous.

#### Discreditation

Maskelyne's type specimen (BM 44213) from the British Museum (Natural History) was reexamined. Andrewsite occurs as rounded encrustations and spherules up to 4 mm in diameter on the specimen studied. The cores of these spherules are composed of barbosolite and goethite. Andrewsite forms as the outermost part of these fibrous, radial, spherulitic aggregates. The surfaces of the spherules are covered with a thin, lustrous film of green platy crystals, and these are in turn coated, irregularly and sparsely, by crystals of cuprite, Cu, and small masses of goethite. Andrewsite is medium to dark green in color, and some is bluish green. A spectacular photograph of andrewsite from this assemblage was recently published by Embrey and Symes (1987).

Optical examination of type andrewsite in oil immersion shows it to be an intimate mixture of acicular, radial rockbridgeite and fibrous-to-platy green crystals of hentschelite, CuFe<sub>3</sub><sup>2+</sup>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>, which was first described by Sieber et al. (1987). Type andrewsite also was examined by X-ray powder diffraction using a Gandolfi camera with a diameter of 114.6 mm, a polycrystalline sample, and exposures of 72 h employing Mn-filtered FeK $\alpha$  X-radiation. Long-exposure powder diffraction patterns confirm hentschelite and rockbridgeite as the principal components of the mixture. Additionally, small amounts of associated minerals, such as chalcocyanite, goethite, and cuprite, may be contained within parts of the rockbridgeite-hentschelite mixture. The fine-grained green patina on the surface of the spherules is a mixture of hentschelite and minor chalcocyanite. It is apparent that Claringbull and Hey based their crystallographic work on a crystal of rockbridgeite.

Type andrewsite was chemically analyzed using an ARL-SEM-Q electron microprobe with an operating voltage of 15 kV and a sample current of 0.025  $\mu$ A, measured

on brass. The standards used were cuprite (Cu), hornblende (Na,Al), and maricite (Fe,P). The spherules have Fe-rich cores; the rims are Cu-enriched. Microprobe analyses indicate that the rockbridgeite component of the mixture is of nearly end-member composition (only 0.5 wt%  $\text{Al}_2\text{O}_3$  and 0.3 wt% CuO). The hentschelite component varied in its Cu/Fe ratio; analyses of high-Cu and low-Cu areas yielded, respectively,  $\text{Al}_2\text{O}_3$  1.5, 1.0;  $\text{Fe}_2\text{O}_3$  42.2, 50.0; CuO 17.0, 10.2;  $\text{P}_2\text{O}_5$  34.5, 34.0;  $\text{H}_2\text{O}$  (by difference) 4.8, 4.8; total = 100.0, 100.0 wt%.

Andrewsite is thus formally discredited as a mixture of hentschelite and rockbridgeite. Had the discreditation taken place prior to the description of hentschelite, then by tradition the name andrewsite could have been assigned to the then-unique component of the original mixture. However, in this case, hentschelite was already established with a complete description and has been reported from a second occurrence (Birch and Mumme, 1988). The name andrewsite thus enters the lexicon of discredited mineral names, this discreditation having been approved by the Commission on New Minerals and Mineral Names. It is with sincere regret that the conclusions of Maskelyne, Claringbull, and Hey in this matter are discredited.

## LAUBMANNITE

### Introduction

Laubmannite was first described by Frondel (1949) using a specimen from Shady, Polk County, Arkansas. Frondel (1949) defined laubmannite as  $(\text{Fe},\text{Mn},\text{Ca})_3\text{Fe}_2^+(\text{PO}_4)_4(\text{OH})_{12}$  and suggested it was related to andrewsite on the basis of similar X-ray powder photographs obtained from two specimens thought to be authentic andrewsite. However, the true nature of andrewsite was unknown at that time. As noted above, Frondel's "andrewsite" specimens (HMM nos. 88105 and 80621) have been reexamined as part of this study and found to be dufrenite, which also occurs at the West Phoenix mine, Cornwall, England, the type locality for andrewsite. The chemical composition of laubmannite had been used to set it apart from other species, although its close relation to dufrenite was evident.

Mrose (1955) stated that "dufrenite, andrewsite, and laubmannite are isostructural if, indeed, not the same mineral." She gave unit-cell data for dufrenite but no information on laubmannite or andrewsite. Presumably, her suggested isostructural relation between andrewsite and laubmannite was drawn in part from Frondel's (1949) paper; it apparently could not have been the result of an examination of type andrewsite, here shown to be a mixture of hentschelite and rockbridgeite.

Moore (1965), gave an orthorhombic unit-cell and space group ( $a = 13.91$ ,  $b = 30.60$ ,  $c = 5.15$  Å, *Pbma*) and a new formula  $[\text{Fe}_2(\text{OH})_{15}(\text{PO}_4)_4]$  for his "laubmannite." However, his material is not laubmannite as then defined either by the type material of Frondel or by Frondel's

description. The source of this confusion about Moore's "laubmannite" was given, in part, by Moore (1970), who stated:

During the course of this study, a new locality was discovered, the laubmannite occurring as bright yellow-green aggregates and affording a powder pattern virtually identical with the Arkansas material. The location is Leveaniemi in the Svappavaara mining district, Norrbotten Province, Sweden. . . . Single crystals of Arkansas laubmannite were obtained from specimens I personally collected and from specimens of a cotype collected and kindly donated by Mr. A. Kidwell.

In discussing his powder data, Moore states:

The laubmannite data do not agree at all with the previously reported pattern of Frondel (1949). Frondel's data are very similar to those for dufrenite, suggesting inadvertent powder contamination of that mineral. One might propose that type laubmannite is not a valid species, but merely a variety of dufrenite, while my mineral is deserving of a new name. However, Frondel's published chemical analysis and proposed molecular formula do not conform with any dufrenite formula or computation based on its cell criteria. On the other hand, his laubmannite analysis conforms well with the cell criteria obtained for [Moore's] Arkansas material [by Moore]. Since chemical analysis usually requires a substantial quantity of material, it is probably based on true laubmannite, whereas the powder study [of Frondel] was performed on adjacent dufrenite.

Thus, much confusion has existed over what laubmannite was and is. Mrose (1955) was in part correct in that laubmannite as then understood was very similar to dufrenite. The "cotype" "laubmannite" from Arkansas, given to Dr. Moore by Dr. Kidwell (Moore, 1970), was not laubmannite as then defined (and therefore no cotype) but is a specimen of a unique, and as yet undescribed, species. Inasmuch as the unique Arkansas material described by Moore (1970) is visually similar to dufrenite and impure laubmannite, the visual confusion is explicable, but the designation "cotype" is, and was, incorrect. Moore's Swedish material, which is identical with Moore's Arkansas material, is not and was not laubmannite either.

Thus, the name laubmannite was attached to a unique, still undescribed mineral from Arkansas and Sweden. This naming of the unique mineral as laubmannite (Moore, 1970) was without the approval of the Commission on New Minerals and Mineral Names, I.M.A., and therefore has no claim to validity or priority.

### Discreditation

The laubmannite type specimens of Frondel (1949) (Harvard Mineralogical Museum no. 100797 and U.S. National Museum no. NMNH 86134) were reexamined. They are part of a typical specimen of banded, fibrous, radial iron-phosphates and fit Frondel's (1949) description well. They were once part of a whole specimen, as

shown by the fact that they have contact surfaces in common and can be rejoined. Indeed, for the assemblage to be described both are needed; the Harvard specimen exhibits mineralization older in sequence than altered laubmannite, and the U.S. National Museum specimen exhibits mineralization younger than altered laubmannite.

The complex sequence of mineralization, as deduced from thin-section and hand-specimen observations, begins with a banded dufrenite-kidwellite-beraunite mixture (fresh laubmannite), followed by a 1-mm band of opaque brown material, which is amorphous to X-rays except for very weak goethite reflections. This is in turn followed by a band 8 mm thick of altered dufrenite-kidwellite with minor beraunite (altered laubmannite), followed by a thin, light green band of dufrenite. Next in sequence is reddish black, bladed rockbridgeite, covered in turn with greenish brown, granular rockbridgeite. These are followed in sequence by layers of goethite alternating with dufrenite-kidwellite-beraunite (laubmannite) and, finally, a green layer of clean dufrenite.

The material corresponding to the laubmannite of Frondel was examined by powder X-ray diffraction, employing the methods described above for andrewsite. The X-ray data indicate that fresh laubmannite is a mixture of beraunite, dufrenite, and minor kidwellite. The 8-mm band of altered laubmannite is a mixture of dufrenite, beraunite, and much kidwellite. Such mixtures are not readily apparent on short-exposure films and are only apparent after long exposures. The powder X-ray data of Frondel are very similar to those of dufrenite but suggest a weak exposure in which only the strongest reflections were recorded. The optical properties given by Frondel (1949) for laubmannite are well within the range of values reported for dufrenite (assuming a beraunite grain was used for the observation of  $2V$ ), and the hardness ( $3\frac{1}{2}$ –4) and density ( $3.33\text{ g/cm}^3$ ) are likewise very similar to those of dufrenite ( $3\frac{1}{2}$ – $4\frac{1}{2}$  and  $3.10$ – $3.34\text{ g/cm}^3$ , respectively).

Type laubmannite was analyzed using microprobe techniques as described above for andrewsite. The mixture of dufrenite and beraunite is an intimate one. The mixture, however, is too intimately intergrown with beraunite, or too altered to kidwellite, to permit good analyses. However, the beraunite component was found qualitatively to be an iron phosphate. The alteration of dufrenite to kidwellite is pervasive.

Thus, the type laubmannite of Frondel (1949) is regretfully discredited as a variable mixture of dufrenite, kidwellite, and beraunite. The discreditation has been approved by the Commission on New Minerals and Mineral Names.

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#### REFERENCES CITED

- Birch, W.D., and Mumme, W.G. (1988) Hentschelite and perloffite from the Spring Creek Copper Mine, South Australia. *Mineralogical Magazine*, 52, 408–411.
- Claringbull, G.F., and Hey, M.H. (1958) A re-examination of andrewsite. *Mineralogical Magazine*, 32, xlv (title only; abstract in notice (no. 100) of Mineralogical Society Meeting, January 23, 1958).
- Collins, J.H. (1876) Note on new minerals from West Phoenix Mine, and from St. Agnes. *Mineralogical Magazine*, 1, 11–15.
- Embrey, P.G., and Symes, R.F. (1987) Minerals of Cornwall and Devon. The British Museum (Natural History), London, and the Mineralogical Record, Inc., Tucson, Arizona, 154 p.
- Foster, C.LeN. (1875) On the place and mode of occurrence of the mineral andrewsite. *Transactions of the Royal Geological Society of Cornwall*, 9, 163–164.
- Frondel, C. (1949) The dufrenite problem. *American Mineralogist*, 34, 513–540.
- Kingsbury, A.W.G. (1952) New occurrences of rare copper and other minerals. *Transactions of the Royal Geological Society of Cornwall*, 18, 386–406.
- (1957) Rockbridgeite from Cornwall and Devon. *Mineralogical Magazine*, 31, 429–430.
- Maskelyne, N.S. (1871) On andrewsite. *Chemical News*, 24, no. 614, 99.
- (1875) On andrewsite and chalkosiderite. *Journal of the Chemical Society of London*, 28, 586–591.
- Moore, P.B. (1965) Basic iron phosphates: A crystallochemical principle. *Science*, 164, 1063–1064.
- (1970) Crystal chemistry of the basic iron phosphates. *American Mineralogist*, 55, 135–169.
- Mrose, M. (1955) Problems of the iron-manganese phosphates. *Geological Society of America Bulletin*, 66, 1660.
- Sieber, N.H.W., Tillmanns, E., and Medenbach, O. (1987) Hentschelite,  $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$ , a new member of the lazulite group, and riechenbachite,  $\text{Cu}_2(\text{PO}_4)_2(\text{OH})_4$ , a polymorph of pseudomalachite, two new copper phosphate minerals from Riechenbach, Germany. *American Mineralogist*, 72, 404–408.

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