

Charlesite, a new mineral of the ettringite group, from Franklin, New Jersey

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Abstract

Charlesite, ideally $\text{Ca}_6(\text{Al},\text{Si})_2(\text{SO}_4)_2(\text{B}(\text{OH})_4)(\text{OH},\text{O})_{12}\cdot 26\text{H}_2\text{O}$ is a member of the ettringite group from Franklin, New Jersey, and is the Al analogue of sturmanite. Chemical analysis yielded CaO 27.3, Al_2O_3 5.1, SiO_2 3.1, SO_3 12.8, B_2O_3 3.2, H_2O 48.6, sum = 100.1 percent. Charlesite is hexagonal, probable space group $P31c$, with $a = 11.16(1)$, $c = 21.21(2)\text{\AA}$. The strongest lines in the X-ray powder diffraction pattern (d , h / l o, hkl) are: 9.70, 100, 100; 5.58, 80, 110; 3.855, 80, 114; 2.749, 70, 304; 2.538, 70, 126; 2.193, 70, 226/404. Charlesite occurs as simple hexagonal crystals tabular on {0001} and has a perfect {10 $\bar{1}$ 0} cleavage. The density is 1.77 g/cm³ (obs.) and 1.79 g/cm³ (calc.). Optically, charlesite is uniaxial (–) with $\omega = 1.492(3)$ and $\epsilon = 1.475(3)$. It occurs with clinohedrite, ganophyllite, xonotlite, prehnite, roebblingite and other minerals in several parageneses at Franklin, New Jersey. Charlesite is named in honor of the late Professor Charles Palache.

Introduction

An ettringite-like mineral was first described from Franklin, New Jersey by Hurlbut and Baum (1960). They noted that it contained boron and silica but, because it conformed closely to ettringite, they preferred to consider it a variety of ettringite. The recent characterization of sturmanite (Peacor *et al.*, 1983) provided insights into the complex substitutions in members of the ettringite group and our recalculation of Ito's analysis (*in* Hurlbut and Baum, 1960) indicated that the Franklin material was not ettringite, but the aluminum analogue of sturmanite. We have named this mineral charlesite in honor of Charles Palache (1869–1954) in recognition of his immense contributions to mineralogy and crystallography. It is particularly fitting that this mineral comes from Franklin, New Jersey, the subject of Palache's famous monograph, *The Minerals of Franklin and Sterling Hill, Sussex County, New Jersey* (Palache, 1935). The mineral and the name

were approved, prior to publication, by the Commission on New Minerals and Mineral Names, I. M. A. The holotype specimen was divided into three portions. One of these is in the type collection at the Smithsonian Institution under catalog # NMNH 148689. A second portion, studied by Hurlbut and Baum (1960) is in the Harvard collection under catalog # 107733. The third portion is in the mineral collection of one of the authors (JLB). Cotype specimens are designated in the text.

Physical and optical properties

Charlesite is transparent with a white streak. The {10 $\bar{1}$ 0} cleavage is perfect and easily produced. The Mohs hardness is approximately 2½. The density reported by Hurlbut and Baum (1960) is 1.77 g/cm³, which compares very well with the calculated value of 1.79 g/cm³. The luster is vitreous on cleavage and fracture surfaces. Charlesite is brittle.

Charlesite was optically examined at 21°C using a spindle stage and Na light. The refractive-index liquids were calibrated using an Abbé refractometer. Charlesite is uniaxial (–) with indices of refraction $\omega = 1.492(3)$ and $\epsilon = 1.475(3)$ for the holotype specimen. Because sturmanite (Peacor *et al.*, 1983) has sectorial zoning with a change of optic sign in the cores of the crystals we carefully checked for evidence of a similar zoning in charlesite, but found none. The crystals are uniaxial (–) throughout. Charlesite is colorless in all specimens examined. Calculation of the Gladstone–Dale relationship, using the constants of Mandarino (1981), yields values of $K_C = 0.271$ and $K_P = 0.274$, which indicate excellent agreement of the data using the compatibility index of Mandarino (1979). Charlesite exhibits a very weak light-violet or light-green fluorescence in short-wave ultraviolet radiation and a much weaker response in long-wave ultraviolet. There is no discernible phosphorescence. Surficial alteration of some crystals results in an opaque layer which exhibits moderate violet fluorescence.

Morphology

Charlesite occurs as hexagonal, euhedral to subhedral crystals, tabular on {0001}. Hurlbut and Baum reported only one form, {10 $\bar{1}$ 2}, but Berry (1963) showed that Hurlbut and Baum's reported *a* cell parameter was double the true value of 11.13Å, which is in good agreement with the value obtained herein. With this value of *a*, the observed form is indexed as {10 $\bar{1}$ 4} and we have observed no additional forms. We note that this form also occurs prominently on sturmanite. Crystals on the holotype sample are rounded and partially dissolved, but those from another Franklin occurrence are sharp and euhedral. We note that sturmanite and charlesite, both having boron substitution for sulfur, have tabular morphology as well, whereas other isostructural species such as ettringite, bentorite, and thaumasite, have been described as

having elongate prismatic habits. A crystal drawing of charlesite was given by Hurlbut and Baum (1960) in this journal and is therefore not reproduced here. A typical charlesite crystal from the roebblingite-bearing assemblage is shown in Figure 1.

X-ray crystallography

According to Hurlbut and Baum (1960), the crystals that they studied, (which we now define as the mineral charlesite) gave rotation and Weissenberg photographs which showed that it is hexagonal with $a = 22.28(1)$ and $c = 21.29\text{Å}$. Berry (1963) showed that *a* should be halved.

Our single-crystal X-ray diffraction data for charlesite are similar to those of other members of the ettringite group, for which all reflections having $l = 2n + 1$ are very weak. Indeed, we were unable to detect reflections for which $l = 2n + 1$ using our selected crystals. However, as Hurlbut and Baum showed that $c = 21.29\text{Å}$ (including the superstructure reflections) using crystals of charlesite, and because other members of the ettringite group have approximately that value of *c*, we presume Hurlbut and Baum's value is correct. The absence of the superstructure reflections in our material may simply be due to disorder of the superstructure in the particular crystals studied. The value of *a* of approximately 11.14Å was verified by our work. The final lattice parameters, obtained by least-squares refinement of Gandolfi data (114.6 mm diameter camera, CuK α X-radiation, Si as an internal standard, polycrystalline sample) are $a = 11.16(1)$ and $c = 21.21(2)\text{Å}$. The powder data are listed in Table 2.

The space group of ettringite was determined by Moore and Taylor (1970) to be $P31c$. However, they note that ettringite frequently displays diffraction symmetry consistent with space group $P6_3/mmc$. Furthermore, they state that this symmetry is the result of twinning or disorder (they favor the latter) and imply that such crystals would give very weak X-ray reflections for which $l = 2n + 1$. The apparent hexagonal symmetry and the lack of observable reflections for which $l = 2n + 1$ in charlesite are both compatible with such twinning or disorder. Because charlesite is isostructural with ettringite, we assume that it has the same space group, $P31c$. No data are inconsistent with this assumption. However, the determination of this space group depends in large part on observing reflections for which $l = 2n + 1$, and even then the diffraction symmetry is consistent with space groups $P6_3/mmc$, $P\bar{6}2c$ or $P6_3mc$. The space group is therefore somewhat problematical.

Chemical composition

Charlesite was chemically analyzed by the late Jun Ito. His data, from Hurlbut and Baum (1960), are reprinted herein as Table 1, and represent a wet-chemical analysis of 800 mg of colorless crystals. Calculation of unit cell contents for this analysis, using the observed density and the newly determined unit-cell parameters yields: Ca_{11.87}

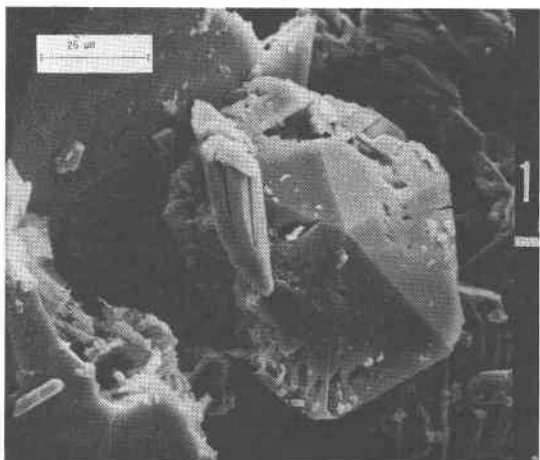


Fig. 1. SEM photomicrograph of typical charlesite hexagonal dipyramidal crystals.

Table 1. Chemical analysis of charlesite

	Franklin, New Jersey*	Theory**
CaO	27.3	27.19
Al ₂ O ₃	5.1	8.24
SiO ₂	3.1	
SO ₃	12.8	12.94
B ₂ O ₃	3.2	2.81
H ₂ O	48.6	48.82
Total	100.1	100.00

* Analysis by Jun Ito in Hurlbut and Baum (1960), includes trace of CO₂

** Theory for Ca₆Al₂(SO₄)₂(B(OH)₄)(OH, O)₁₂·26H₂O.

(Al_{2.44}Si_{1.26})Σ3.70(SO₄)_{3.90}(B(OH)₄)_{2.24}(OH_{21.94}O_{2.06})Σ24.00·50.33H₂O. This is in good agreement with the theoretical formula Ca₆(Al, Si)₂(SO₄)₂(B(OH)₄)(OH, O)₁₂·26H₂O, with Z = 2.

This assignment of hydrogen to three different sites is based on the following three steps. (1) Boron was assumed to be present as (B(OH)₄) tetrahedral groups. This assignment is not based on any direct data for this specific coordination but is based on reasonable analogy with other boron minerals, in combination with consistency with overall charge balance. (2) The value of 21.94 (OH) per cell which is not coordinated to B was calculated assuming overall charge balance for the full formula and with the restriction that Σ(O + OH) = 24.00 atoms, as required by the crystal structure. (3) H₂O was calculated for that hydrogen not assigned to (B(OH)₄) or (OH). The apparent discrepancy in the H₂O content (1.67 H₂O less than the full 52 H₂O required by the ideal structure) is not serious. This is explained, in part, by the two roles played by H₂O in the structure. First, there are 48 H₂O per cell associated with Al(OH)₆ octahedra and Ca ions coordinated by 4 (OH) and 4 H₂O which form columns parallel to the c-axis (Taylor, 1973; Moore and Taylor, 1970). Second, channels between columns are occupied by (SO₄), (B(OH)₄) and (2H₂O) groups which must sum to 8 per unit cell, assuming full occupancy. For charlesite, the sum of (SO₄), (B(OH)₄) and that H₂O in excess of the 48.0 H₂O coordinated to Ca is 8.47, well within the standard errors of chemical analysis, especially on such a highly hydrated mineral.

The unusual substitution of Si for Al on an octahedrally coordinated site is validated by its presence in thaumassite, another member of the ettringite group, but the site is still principally occupied by Al. Sturmanite has the idealized chemical formula Ca₆(Fe³⁺, Al, Mn²⁺)₂(SO₄)₂(B(OH)₄)(OH, O)₁₂·25H₂O. Sturmanite and charlesite are similar in Ca, S, B and H contents, differing in the composition of the octahedrally coordinated sites.

Charlesite is therefore the aluminum analogue of sturmanite.

Occurrence

Charlesite was found in late 1945 by miners in the Franklin Mine in Franklin, Sussex County, New Jersey, and was brought to the attention of one of the authors (JLB). This initial discovery was reported by Hurlbut and Baum (1960) and they provided a sketch-map which included the vein in which charlesite occurred. It was located immediately above the 800 level, about 15 feet into the ore from the hanging wall, and close to the north side of the Palmer shaft pillar. The ore consists of franklinite and willemite with minor andradite and moderately abundant mica, likely of phlogopite/hendricksite composition. This primary assemblage is unevenly coated with a dark brown layer of grossular which is coated, in turn, with a fine-grained impure mixture consisting, for the most part, of a ganophyllite-like mineral of unknown composition. Subsequent crystallization produced a thick druse of ganophyllite, (K, Na, Ca)₂Mn₈(Si, Al)₁₂(O, OH)₃₂(OH)₄·8H₂O (Dunn *et al.*, 1983) in crystals up to 2.0 mm intergrown with second-generation willemite and minor rhodonite, both of which are euhedral. These three minerals are unevenly coated with a Mn-chlorite and pectolite. Continued crystallization resulted in the growth of euhedral, colorless, transparent charlesite crystals up to 6.0 mm, which appear to have formed contemporaneously with large (12 mm) superb crystals of clinohedrite, CaZn SiO₃(OH)₂. These minerals were followed in the crystallization sequence by very small fascicles of pectolite and

Table 2. X-ray powder diffraction data for charlesite

d(Obs)	d(Calc)	hkl	I/I ₀ *	d(Obs)	I/I ₀
9.70	9.66	100	100	1.749	20
5.58	5.58	110	80	1.693	10
4.936	4.938	112	20	1.663	5
4.654	4.648	104	40	1.606	20
3.855	3.843	114	80	1.563	30
3.573	3.571	204	30	1.500	20
3.444	3.454	212	40	1.480	2
3.230	3.221	300	10	1.448	5
2.996	3.005	214	10	1.380	1
	2.986	116		1.327	2
2.749	2.753	304	70	1.295	5
2.666	2.680	310	20	1.269	2
	2.651	008		1.252	2
2.598	2.599	312	20	1.241	2
2.538	2.540	126	70	1.215	1
2.470	2.469	224	1	1.205	1
2.391	2.392	134	5	1.184	1
2.325	2.324	208	2	1.166	5
2.193	2.199	404	70	1.125	5
	2.190	226		1.096	5
2.133	2.136	136	50		
2.044	2.047	308	5		
	2.045	324			
1.991	1.995	406	1		
1.956	1.960	414	1		
1.926	1.922	228	20		
1.884	1.885	318	1		
1.837	1.834	12, 10	10		
	1.832	352			
1.787	1.786	408	5		

Table 3. Composition and cell parameters for members of the ettringite group

SPECIES	COMPOSITION				a (Å)	c (Å)	Reference
ETTRINGITE	Ca ₆	Al ₂	(SO ₄) ₃	(OH) ₁₂ · 26H ₂ O	11.23	21.44	Taylor (1973)
BENTORITE	Ca ₆	(Cr, Al) ₂	(SO ₄) ₃	(OH) ₁₂ · 26H ₂ O	22.35	21.41	Gross (1980)
STURMANITE	Ca ₆	(Fe ³⁺ Al) ₂	(SO ₄) ₂ (B(OH) ₄)	(OH) ₁₂ · 26H ₂ O	11.16	21.79	Peacor <i>et al.</i> (1983)
CHARLESITE	Ca ₆	(Al, Si) ₂	(SO ₄) ₂ (B(OH) ₄)	(OH) ₁₂ · 26H ₂ O	11.16	21.21	present study
THAUMASITE	Ca ₆	Si ₂	(SO ₄) ₂ (CO ₃) ₂	(OH) ₁₂ · 24H ₂ O	11.04	10.39	Edge and Taylor (1971)
JOURAVSKITE	Ca ₆	Mn ₂	(SO ₄) ₂ (CO ₃) ₂	(OH) ₁₂ · 24H ₂ O	11.06	10.50	Granger and Protas (1969)

colorless acicular crystals of xonotlite, the latter of which appear to grow preferentially on charlesite. The above description is of the cotype, NMNH C6247.

The other cotype specimen, NMNH C6401, is probably of a very closely related paragenesis, but exhibits different mineralogy. This assemblage consists of willemite/franklinite ore coated with a second generation of bright green, prismatic willemite crystals up to 20 mm. Some willemite has been partially dissolved, leaving light orange vugs and molds formed of granular grossular which is coated with euhedral hancockite. Charlesite crystals (Fig. 1) occur as colorless, water-clear, euhedra in vugs among the willemite crystals and also filling cracks in fractured willemite. These willemite crystals are coated with a Mn-chlorite and, in turn, by pearly-white prehnite. Some interstices among these coated crystals are filled with granular clinohedrite. The entire assemblage is covered by a druse of granular datolite, followed by massive roeblingite, (Ca,Sr)₁₂(Mn,Ca)₂Pb₄(SO₄)₄Si₁₂O₂₈(OH)₂₀ (Dunn *et al.*, 1982).

Yet another distinct assemblage was noted by two miners, Harold and Kenneth Stanaback, and presented to one of the authors (JLB). This assemblage provided the holotype specimen. It consists of franklinite ore with very minor willemite, which is encrusted with a 1–5 cm layer of vuggy, recrystallized datolite, manganaxinite, prehnite and hancockite. This irregular layer is, in turn, coated with ganophyllite, followed by a layer of extremely fine-grained Mn-chlorite. Subsequent crystallization gave rise to white, pearly prehnite, followed by sparse barite and, in turn, abundant clinohedrite and charlesite. In this assemblage, the charlesite crystals have a dull luster, are slightly white and, in some cases, cavernous and partially dissolved.

Although these parageneses have some minerals in common, the diversity of textures and ore-relationships suggests some degree of spatial separation of the occurrences. Although the Franklin deposit is low in sulfur on a gross scale, a number of sulfide and sulfate minerals are known in small amounts and barite may have been quite common locally. Hence, charlesite might have been more common than the present paucity of preserved specimens indicates, and may have been overlooked if it occurred

with non-fluorescent minerals inasmuch as much casual collecting by miners was influenced by the fluorescence of many species, thus imparting a bias to what was preserved.

Relation to other members of the ettringite group

The description of charlesite, together with the recent descriptions of sturmanite (Peacor *et al.*, 1983) and bentorite (Gross, 1980), brings the ettringite group to six species having 24–26 H₂O (Table 3). In addition to these, there are three closely related compounds: despujolsite, Ca₆Mn₂⁴⁺(OH)₁₂(SO₄)₄·6H₂O; schaurteite, Ca₆Ge₂(OH)₁₂(SO₄)₄·6H₂O; and fleischerite, Pb₆Ge₂(OH)₁₂(SO₄)₄·6H₂O, all of which have less water and have a between 8.5 and 8.9 Å, as contrasted with a value of approximately 11 Å for the species in Table 3. There are also other isostructural phases which have been synthesized (Taylor, 1973) but are not known to occur naturally.

Acknowledgments

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