# Bjarebyite, (Ba, Sr)(Mn,Fe,Mg) $_2$ Al $_2$ (OH) $_3$ (PO $_4$ ) $_3$ , A New Species

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# INTRODUCTION

The Palermo No. 1 pegmatite, near North Groton, New Hampshire, is famous for an extraordinarily long list of mineral species, of which no less than 50 phosphate species have been reported, about 60% of all known pegmatite phosphates (Moore, 1973). This apparently has resulted from a series of retrograde reactions, such as metasomatic and hydrothermal reactions over a range of temperatures upon primary phosphate giant crystals such as triphylite, graftonite and amblygonite. From the triphylite, low temperature oxidative reactions led to a large number of secondary phosphate hydrates such as laueite, strunzite and phosphosiderite. Where reducing conditions prevailed, ferrous phosphate hydrates arose such as ludlamite, phosphoferrite and vivianite, the reducing environment indicated by the presence of coexisting late sulfides. Hydrothermal attack upon amblygonite led to augelite, wardite and crandallite. Exchange reactions between triphylite and adjacent amblygonite produced compounds such as scorzalite and childrenite. Introduction of  $Ba^{2+}$  and  $Sr^{2+}$ at this stage resulted in such exotica as palermoite and bjarebyite, the latter a new species and the subject of this paper.

#### PARAGENESIS

We feel that a detailed account of the bjarebyite paragenesis is justifiable even though the species is at present most rare with but a few crystals discovered. This is because the Palermo pegmatite has received much attention from collectors and many examples of this paragenesis have been seen by the senior author in private collections suggesting that bjarebyite may be "discovered" in many collections upon closer scrutiny.

The type specimen was collected in 1947 by the late Mr. Gunnar Bjareby and bears the label "Dickinsonite (ND = (not determined)), No. 2260". The sample, originally 4 x 4 x 5 cm, was broken into four pieces to provide enough material for study. The mineralogy is extraordinarily complex and includes the species amblygonite, augelite, childrenite, siderite, scorzalite, quartz, minor sulfides, Fe-Mn oxides, bjarebyite and palermoite. It derived from a small metasomatized amblygonite-scorzalite pod which probably occurred in close association with triphylite crystals. Hydrothermal reaction at intermediate temperature would lead to exchange of cations between the triphylite and am-

blygonite to form scorzalite followed by augelite, childrenite and siderite. Such products appear brecciated and the mass has a nodular outline distinct from the subhedral outline of the parent phases. Bjarebyite and palermoite occur at the final stages as crystals in open cavities along the contact between the amblygonite-scorzalite remnants and the Fe-Mn oxides. Palermoite specimens show a similar paragenesis suggesting that bjarebyite may occur in close association with this mineral.

### PHYSICAL PROPERTIES

The color of bjarebyite is emerald green with a faint bluish tinge, darker than ludlamite and brazilianite which the species closely resembles. It always appears as highly faceted and very complex crystals, usually pitted and etched. The luster is subadamantine, hardness  $4^+$  on Mohs scale, streak white. Two perfect cleavages,  $\{010\}$  and  $\{100\}$ , distinguish it from ludlamite and brazilianite. In addition, the ludlamite paragenesis is usually confined to a stage directly replacing triphylite, a primary phase which is absent in this sample.

#### CRYSTAL MORPHOLOGY

Crystals are lustrous, eminently suitable for reflection goniometry and range up to 3mm in greatest dimension. We examined three crystals and constructed an indexed gnomogram consistent with the structure cell derived from X-ray study. The crystals are spear-shaped and steeply terminated.

The crystal class is monoclinic holosymmetric (2/m) with c {001}, a {100}, b {010}, m {110}, d {120}, r {111}, f {121}, e {131}, h {141}, w {411}, l {211}, t {021}, q {011}, and v {031}. Of the 14 distinct forms 11 occur among the 23 entries of descending d-spacings. Six forms of the longest d-spacings are present but further down the list, all negative forms are missing, although the reticular hypothesis would predict their presence. This contradiction may have resulted from our selection of crystals all of which were attached to matrix and had to be broken, fortuitously destroying negative forms. Accordingly, missing negative forms (such as {101}, {111}, {121}, {211}, {221} and {131}may actually prove to be present as other crystals are discovered, suggesting that bjarebyite crystals may be very complex indeed.

A plan and clinographic projection of the bjarebyite





a

r

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# FIGURE LEGEND

Fig. 1. Crystal of bjarebyite showing the forms c (001),  $a \{100\}, b \{010\}, m \{110\}, d \{120\}, r \{111\}, f \{121\}, e \{131\},$ h {141}, w {411}, l {211}, t {021}, q {011}, and v {031}. Palermo No. 1 mine.

B. Clinographic projection

C. Plan, orthoaxis polar

Table 1	. Bjarebyite. Structure Cell Parameters
a (Å)	8.930(14)
b (Å)	12.073(24)
c (Å)	4.917(9)
β	100.15°(0.13°)
$V\left( {\mathop{ m A} olimits}{3}  ight)$	521.8(1.5)
space group	$P2_1/m$
formula	$(Ba,Sr)(Mn,Fe,Mg)_2 Al_2(OH)_3[PO_4]_3$
Z	2

development appears in Fig. 1. The plan with the *b*-axis polar reveals the spear-shaped character of the crystals and shows the extent of their complexity.

# X-RAY CRYSTALLOGRAPHY

Single crystal Weissenberg and rotation photographs about the *b*- and *c*-axes and a thorough three-dimensional crystal structure analysis ( $\mathbf{R} = 0.06$ ) established the cell shape and the details of the atomic arrangement, the latter to be published elsewhere. The cell data are offered in Table 1. A few small crystal fragments were crushed and rolled into a sphere of powder with rubber cement. The powder data in Table 2 were obtained by matching strong single crystal intensities with the interplanar spacings and these results were refined by least squares fitting.

The atomic structure of bjarebyite not only establishes its formula with certainty but reveals a new kind of  $AlO_6$ octahedral polymerization: octahedral edge-sharing dimers further link via opposite corners to form an infinite  $[A1_2O_6(OH)_3]$  chain.

# CHEMICAL COMPOSITION

Crystals of bjarebyite were submitted to ARL electron microprobe analysis.<sup>1</sup> Elements from Na to U were qualitatively scanned and Mg, Fe, Mn, Al, Ca, Sr, Ba were quantitatively analyzed. P and (OH) were determined from the crystal structure analysis. Likewise, valence states of the cations were obtained from the structure study.

The homogeneous crystal was a fragment of the same crystal used in the structure analysis and its average composition based on a 60 area scan is accepted as the type analysis for bjarebyite. Another rather massive fragment gave a range of compositions in Fe, Mn, Ba and Sr, the other elements being rather constant throughout. The details of the analyses appear in Table 3.

We are committed, on the basis of the structure analysis, to accept a solid solution of Fe and Mn over equivalent positions. Since the sum of large cations =5 for one formula unit, the computed bjarebyite formula is  $(Ba_{1.1}Sr_{0.1})$   $(Mn_{0.9}^{2+}Fe_{0.9}^{2+}Mg_{0.2})Al_{1.8}$  for the cations, with Mn:Fe nearly 1:1. This suggests that a ferrous predominant bjarebyite also exists and, indeed, appears in some of the scans on the massive fragment. Based on the probe and crystal structure analyses, the bjarebyite formula is  $(Ba_{2.1})(Mn,Fe,Mg)_{2}^{2+}$   $Al_{2}(OH)_{3}[PO_{4}]_{3}$  and the name applies to the ideal end-

<sup>1</sup> Performed by Mr. G. R. Zechman of this laboratory.

 Table 2. Bjarebyite. Observed and Calculated Powder

 Data

(Sphere powder mount, 114.6 mm camera diameter, Fe/Mn radiation, calibrated film)

Fe/Mn rac	liation, calibrate	d film)	
I/Io	d(obs)	d(calc)	hkl
7	8.81	8.79	100
4	4.97	4.98	120
2	4.59	4.59	101
4	4.47	4.49	011
1	4.124	4.130	210
2	3.562	3.553	220
1	3.447	3.435	211
1	3.295	3.308	121
	2 000	, 3.094	031
2	3.090	<sup>{</sup> 3.081	221
3	3.024	3.028	131
4	2.910	2.912	211
2	2.852	2.847	310
2	2.811	2.821	131
7	2.681	2.687	221
,		2.662	311
3	2.643	2.636	320
1	2.514	2.523	141
2	2.495	2.487	321
2	2.444	2.446	102
1	2.413	2.420	002
1	2.377	2.369	330
1	2.310	2.298	202
2	2.261	2.257	$\frac{202}{212}$
2	2.177	2.162	410
3	2.137	2.138	151
1	2.090	2.095	122
2	2.039	2.023	312
2	2.009	2.012	060
10	2.010	{ 1.996	232
2	1.956	1.954	132
2	1 880	1.879	222
1	1 786	1.792	$\frac{222}{402}$
1	1,,00	1.772	412
1	1.759	{ 1.758	500
1	1.733	1.740	510
1	1.702	1.697	342
1	1 681	1.677	351
1	1.659	1.665	252
2	1.624	1.611	530
2	1.600	1.596	441
2	1.578	1.566	501
3	1.556	1.554	162
3	1.528	1.517	541
-	1.020	1.497	033
5	1.495	{ 1.476	601
		and	
	about 30 lines	s, each less than 2	

member composition  $BaMn_2 Al_2(OH)_{3}[PO_4]_3$  and all compositions with Ba > Sr and Mn > Fe. Compositionally and structurally, bjarebyite is unique, but is remotely related to the eosphorite-childrenite group and it is suggested the

Table 3. Bjarebyite. Electron Microprobe Analyses											
	Ba	Sr	Ca	Mg	Mn	Fe	Al	Mn/Fe + Mn			
Heterogeneous massive											
Low Ba 10 area scar	n 19.70	2.53	0.06	0.71	6.25	8.65	7.00	0.42			
High Ba 10 area scar	n 22.93	0.25	0.08	0.78	7.44	6.08	7.06	0.55			
Average 60 area scar	n 21.22	1.33	0.08	0.76	7.40	6.74	7.11	0.53			
Homogeneous crystal											
Average 60 area scar	n 21.81	0.79	0.06	0.84	7.15	6.95	7.01	0.51			
BaFeMnAl <sub>2</sub> (OH) <sub>3</sub> [PO <sub>4</sub> ] <sub>3</sub>											
Ideal	21.53	-	-	-	8.60	8.75	8.46	0.50			

species be classified near that group. We also mention that the  $Fe^{3+}>A1^{3+}$  analogue may also exist on structural grounds.

The specific gravity of bjarebyite, determined by Berman microbalance, is  $3.95 \pm 0.02$ . The sample was obtained from a recently collected specimen and afforded a powder pattern identical with type material. We compute  $p(calc) = 4.02 \text{ gm/cm}^3$  from the unit cell and the composition BaMnFeA1<sub>2</sub>(OH)<sub>3</sub>[PO<sub>4</sub>]<sub>3</sub>. A Gladstone-Dale calculation based on the oxide specific refractive energies in Larsen and Berman (1934) gives  $p(calc) = 3.86 \text{ gm/cm}^3$ which is within 4% of the structure cell computation. The specific gravity is much greater than ludlamite (3.2), brazilianite (3.0) and arrojadite (3.6) and serves as an additional diagnostic tool for identification by sink-float techniques in Clerici solution. Its composition suggests that bjarebyite should occur in specimens which contain palermoite, goyazite, and associated eosphorite-childrenite.

#### OPTICAL PROPERTIES

Bjarebyite is biaxial (+),  $2V \sim 35^\circ$ ,  $r \gg v$ , birefringence low with a 1.692,  $\beta 1.695$ ,  $\gamma 1.710$  all  $\pm 0.003$ , weakly pleochroic greyish tan to pale yellow-green. These values vary somewhat depending on the sample composition and we selected a crystal adjacent to the type crystal for this optical study.

#### NAME

The beauty of the crystals, the location and the source of the specimen provide us with the honor of naming the new species BJAREBYITE after the late Mr. Gunnar Bjareby of Boston, a talented artist and naturalist, who assembled a magnificent collection of hand specimens and micromounts, particularly of the New England pegmatites. He amassed a micromount collection of over 1,000 exquisite Palermo specimens and was a phosphate mineral student with extraordinary insight and knowledge. The care and detail of his investigations, unfortunately never published, place Mr. Bjareby among the most outstanding of 20th Century amateur mineralogists.

The species and its name have been approved by the International Commission of New Minerals and New Mineral Names, International Mineralogical Association. The type specimen shall be preserved in the United States Natural History Museum (Smithsonian Institution).

# ACKNOWLEDGMENTS

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#### REFERENCES

- LARSEN, E. S. and H. BERMAN, (1934). The microscopic determination of the nonopaque minerals. U. S. Geol. Surv. Bull. 848, 31.
- MOORE, P. B. (1973). Pegmatite phosphates: descriptive mineralogy and crystal chemistry. *Mineral. Rec.*, 4, 103-130.

#### Note added in proof:

A recent visit (June 23) to the Palermo No. 1 pegmatite by the senior author afforded good specimens of abundant porous whitlockite-carbonate apatite-siderite masses uncovered by resumed mining operations. Bjarebyite occurs in moderate abundance, with colorless striated palermoite prisms and brown lath-like childrenite crystals, as deep bluish green masses of fibrous appearance up to an inch across. Upon closer examination, the masses are seen to be composed of etched highly faceted complex crystals in parallel growth. Masses of scorzalite and amblygonite also occur locally in lustrous green glassy fragments unlike green rockbridgeite which it superficially resembles. About twenty hand specimens of the mineral were culled and we anticipate that more specimens of this species will be found, especially in association with the whitlockite.

In addition, Mr. Curt Segeler recently sent the senior author a micromount specimen of excellent pseudo-rhombohedral crystals of an unknown green mineral. It occurs implanted upon scalenohedral siderite crystals in vuggy pockets and proved by X-ray investigation to be bjarebyite. The crystal development is unusual and bears no simple relationship with our crystal drawings of the type material. Siderite masses in close association with whitlockite should be carefully examined for this magnificent species.

We thank Mr. Peter Samuelson, mine operator, for the opportunity to collect these specimens and Mr. Segeler for his continued assistance in carefully selecting specimens for further study.