

The X-Ray Crystallography of Tavorite from the Tip Top Pegmatite, Custer, South Dakota†

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Abstract

Bright apple green millimeter-sized crystals of tavorite from the Tip Top pegmatite, near Custer, South Dakota are triclinic, space group $P\bar{1}(2)$, with refined unit-cell parameters $a = 5.340(2)$, $b = 7.283(2)$, $c = 5.110(2)$ Å, $\alpha = 109.29(2)^\circ$, $\beta = 97.86(3)^\circ$, $\gamma = 106.32(3)^\circ$, $V = 174.1(3)$ Å³, $a:b:c = 0.7332:1:0.7016$, $Z = 2$, $D(m)$ (suspension in methylene iodide) = 3.32(1) and $D(x) = 3.33$ g/cm³ (for the theoretical formula). A fully indexed X-ray powder pattern is presented. Semiquantitative electron microprobe and secondary ion mass spectroscopic analyses indicate a formula near end-member $LiFe^{+3}(PO_4)(OH)$. The Tip Top tavorite is biaxial positive, $\alpha = 1.795(5)$, $\beta = 1.81(1)$, $\gamma = 1.86(1)$, $2V(meas.) = 50(2)^\circ$, $2V(calc.) = 59^\circ$, $X\Lambda a \approx 15^\circ$, $Y\Lambda b \approx 0^\circ$, and $Z\Lambda c \approx 38^\circ$. There is no evidence for optical absorption, pleochroism or dispersion.

Introduction

Tavorite, ideally $LiFe^{+3}(PO_4)(OH)$, is the ferric-iron analogue of montebasite and is a member of the amblygonite group. It was originally described by Lindberg and Pecora (1955) from the Sapucaia pegmatite mine, Minas Gerais, Brazil where it was found as fine-grained crystalline aggregates. Unfortunately, these aggregates were unsuitable for X-ray single-crystal study; hence the symmetry, space group and unit-cell parameters of natural tavorite were undetermined at that time. The original X-ray powder diffraction data were published by Lindberg and Pecora (1955). The data are listed in the Mineral Powder Diffraction File Data Book 1986 under PDF 10-424 and remain unindexed.

Recently, tavorite crystals of exceptional quality were discovered at the Tip Top pegmatite, near Custer, South Dakota. The physical characteristics of these crystals allowed us to undertake a comprehensive X-ray restudy of this mineral and the results are reported herein.

Occurrence

The studied tavorite [National Museum of Natural History (NMNH) #165334] occurs as millimeter-sized bright apple green crystals within vugs associated with rockbridgeite, jahnsite, vivianite and other phosphates at the Tip Top pegmatite, near Custer, South Dakota. A

typical crystal grouping is shown in Figure 1. The forms observed by single crystal study are {100}, {010} and {001}. Additional information about the locality, paragenesis and, specifically, about tavorite, can be found in Campbell and Roberts (1986).

X-Ray Studies

Two crystals were selected for detailed precession single-crystal study. One was mounted with a^* and the other with b^* parallel to the dial axis. Levels photographed with Zr-filtered Mo radiation were $hk0$, $hk1$, $0kl$, $1kl$, $h0l \rightarrow h2l$.

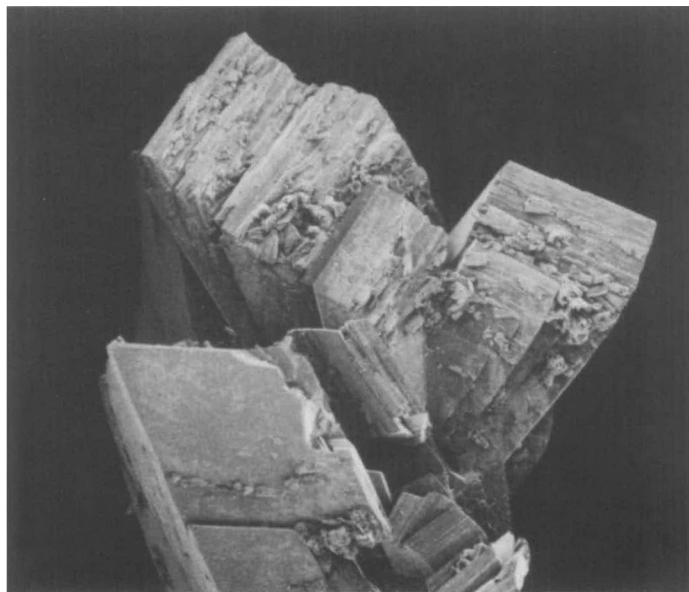


Figure 1. A typical grouping of tavorite crystals.

Tavorite is triclinic, space group choices $P1(1)$ or $P\bar{1}(2)$ (diffraction aspect P^*). The unique space group is most likely $P\bar{1}(2)$ by analogy with that determined by crystal structure analysis on synthetic tavorite by Genkina *et al.* (1984). Fully indexed, 114.6 mm Gandolfi camera, powder film data are presented in Table 1. Refined unit-cell parameters, based on 23 reflections between 3.401 and 1.615 Å for which unambiguous indexing was possible, are given in column 1 of Table 2. Intensities of all indexed reflections were checked on precession films. These cell parameters are in their reduced form as indicated by an in-house cell reduction computer program.

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‡Deceased

Table 1.
X-Ray Powder Data for Tavorite

* $2\theta^{\circ}_{corr.}$	$I_{est.}$	$d(\text{\AA})_{meas.}$	$d(\text{\AA})_{calc.}$	hkl	$2\theta^{\circ}_{corr.}$	$I_{est.}$	$d(\text{\AA})_{meas.}$	$d(\text{\AA})_{calc.}$	hkl
17.311	10	6.44	6.44	010	52.333	15	2.197	2.199	$2\bar{1}\bar{1}$
22.464	60	4.97	4.96	100	52.733	3	2.181	2.183	$2\bar{2}\bar{1}$
23.173	10	4.82	4.83	$1\bar{1}0$	53.734	20	2.143	2.143	$1\bar{2}\bar{2}$
23.440	50	4.77	4.76	011	54.729	10	2.107	2.106	$2\bar{2}\bar{1}$
23.990	60	4.66	4.67	001	55.960	1	2.065	2.065	$1\bar{1}\bar{2}$
28.443	40	3.94	3.93	$10\bar{1}$	57.386	20	2.018	2.107	032
			3.433	$1\bar{1}\bar{1}$	58.261	10	1.990	1.990	$2\bar{0}\bar{1}$
32.745	30	3.436	{ 3.430	111	59.012	10	1.967	1.965	202
33.096	20	3.401	3.398	$1\bar{1}0$	60.123	20	1.931	1.931	$1\bar{0}\bar{2}$
33.896	70	3.323	3.320	021	63.315	10	1.846	1.846	$1\bar{3}\bar{1}$
34.447	100	3.271	3.272	120	64.515	20	1.815	1.815	$1\bar{4}\bar{1}$
			3.230	011	67.417	10	1.745	1.745	041
34.972	10	3.224	{ 3.221	020				1.717	$2\bar{2}\bar{2}$
37.198	90	3.037	3.036	$10\bar{1}$	68.718	30	1.716	{ 1.715	$2\bar{2}\bar{2}$
43.027	10	2.641	2.643	210	69.518	15	1.699	1.699	220
44.678	20	2.549	2.555	$1\bar{2}\bar{1}$				1.660	042
45.053	15	2.528	2.530	012	71.295	15	1.662	{ 1.659	321
46.354	50	2.461	2.463	$2\bar{0}\bar{1}$	71.745	20	1.653	1.653	300
46.954	20	2.431	2.432	$1\bar{2}\bar{1}$	72.220	3	1.644	1.642	$2\bar{2}\bar{2}$
48.105	5	2.377	2.377	022				1.636	240
			2.355	111	72.545	25	1.637	{ 1.636	$1\bar{2}\bar{3}$
			2.353	102	73.721	20	1.615	1.615	022
48.655	25	2.351	{ 2.352	$1\bar{2}0$					
			2.341	$1\bar{3}\bar{1}$					
			2.282	130					
50.382	10b	2.276	{ 2.271	021					

* 114.6 mm Gandolfi camera, Fe radiation Mn filter ($\lambda_{FeK\alpha} = 1.9373 \text{\AA}$)

- Film corrected for shrinkage

- b = broad line

- Intensities visually estimated

- Indexed on $a = 5.340$, $b = 7.283$, $c = 5.110 \text{\AA}$, $\alpha = 109.29^{\circ}$, $\beta = 97.86^{\circ}$, $\lambda = 106.32^{\circ}$

Table 2.
Unit-cell Data for Tavorite, Amblygonite and Montebbrasite in Reduced Cell Form with $c < a < b$

	Tavorite (this study)	Tavorite Genkina <i>et al.</i> (1984)	Amblygonite ⁴ Bauer (1959)	Montebbrasite ⁴ Haapala (1966)
$a(\text{\AA})$	5.340(2)	5.307	5.184(10)	5.175(3)
$b(\text{\AA})$	7.283(2)	7.266	7.031(10)	6.984(3)
$c(\text{\AA})$	5.110(2)	5.138	5.040(10)	5.047(3)
α	$109.29(2)^{\circ}$	108.59°	$109^{\circ}29(15)'$	$108^{\circ}52(5)'$
β	$97.86(3)^{\circ}$	98.02°	$97^{\circ}48(15)'$	$98^{\circ}05(5)'$
γ	$106.32(3)^{\circ}$	107.07°	$106^{\circ}37(15)'$	$106^{\circ}47(5)'$
$V(\text{\AA})^3$	$174.1(3)^{\circ}$	173.5	[160.4]	[159.7]
a:b:c	0.7332:1:0.7016	[0.7304:1:0.7071]	0.7372:1:0.7167	0.7410:1:0.7227
Z	2	2	2	2
Space Group	P1(2) ¹	P1(2)	P1(2)	—
D(m)	$3.32(1)^2$	—	—	3.028(3)
D(x)	3.33 ³	3.33	3.04	3.065

1 By analogy with Genkina (1984)

2 By heavy liquids using methylene iodide

3 For theoretical end-member formula

4 Cell transformation to reduced-cell is $\bar{1}00/011/00\bar{1}$

Note: Values in [] are calculated from cell parameters

Table 2 also contains comparative unit-cell data for synthetic tavorite and the most recent crystallographic data for the other two members of the group, namely, amblygonite, ideally $\text{LiAl}(\text{PO}_4)\text{F}$ (Bauer, 1959) and montebrasite, ideally $\text{LiAl}(\text{PO}_4)(\text{OH})$ (Haapala, 1966). The original cell data have been reduced and transformed to the conventional setting with $c < a < b$ for comparison purposes.

The data obtained from this study are similar to those reported by Genkina *et al.* (1984) but the cell parameters, and consequently the cell volume, are significantly larger than those reported for either amblygonite or montebrasite. This is due to Fe^{+3} for Al^{+3} replacement, since the ionic radius of Fe^{+3} is substantially larger (0.13 Å) than Al^{+3} .

Optical Properties

The two crystals used for the single-crystal study were subsequently used to determine the optical properties. Spindle-stage mounts observed in Na gel filtered light ($\lambda = 589.9$ nm) show that Tip Top tavorite is biaxial positive, $\alpha = 1.795(5)$, $\beta = 1.81(1)$, $\gamma = 1.86(1)$, $2V(\text{meas.}) = 50(2)^\circ$, $2V(\text{calc.}) = 59^\circ$, $X\Lambda a \approx 15^\circ$, $Y\Lambda b \approx 0^\circ$, $Z\Lambda c \approx 38^\circ$. There is no evidence for absorption, pleochroism or dispersion.

Composition

The Tip Top crystals were verified as tavorite both by X-ray powder diffraction and single crystal study and by electron microprobe and ion microprobe mass spectroscopic methods. Type Brazilian tavorite (NMNH 106842), a light green highly porous material, and the tavorite crystals from the Tip Top pegmatite were examined by electron microprobe methods and were found to contain major Fe and P. Other elements, known to occur in the same geochemical environment, were sought but not found. The two specimens have nearly identical compositions; Mn was found in trace amounts, and Na and F are both absent. Because of Li boil-off and the physical nature of the type specimen, determinations for Fe and P are considered to be semiquantitative and are not accurate enough for publication.

As a check on the lithium content, we employed secondary ion mass spectroscopy (SIMS) analysis in the instrumental form known as the ion microscope and directly compared the type and the new specimens. A primary beam of mass-filtered negative ^{16}O ions was used to sputter the specimens. The positive secondary ions thus produced were first subjected to energy filtering to greatly reduce any possible contribution of molecular ions to the spectrum prior to magnetic mass analysis. The measured secondary ion ratios for the type and new tavorite specimens were:

<i>Type (Brazil)</i>	<i>New (South Dakota)</i>
$7\text{-Li}/31\text{-P} = 20.1$ (rel s = 1%)	$= 19.6$ (rel s = 1%)
$7\text{-Li}/56\text{-Fe} = 0.927$ (rel s = 0.5%)	$= 0.795$ (rel s = 0.6%)

The relative standard deviation, *s*, is calculated from 10 consecutive measurement cycles through the mass peaks.

These Li:P and Li:Fe ratios indicate that the tavorite from both localities are virtually identical in composition.

Theoretical $\text{LiFe}^{+3}(\text{PO}_4)(\text{OH})$ requires $\text{Li}_2\text{O}8.55$, $\text{Fe}_2\text{O}_345.69$, $\text{P}_2\text{O}_540.61$, $\text{H}_2\text{O}5.15$, sum 100.00 wt%. With $Z = 2$ and the cell volume given in column 1 of Table 2, the calculated density is 3.33 g/cm³. This is in excellent agreement with the specific gravity of 3.32(1) measured by suspension of tavorite crystals in methylene iodide.

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