

# Foitite, $\square[\text{Fe}_2^+(\text{Al}, \text{Fe}^{3+})]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ , a new alkali-deficient tourmaline: Description and crystal structure

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## ABSTRACT

Foitite is a new tourmaline species from southern California. It forms bluish black prisms of triangular cross section, elongated along *c* with striations parallel to *c* on the convex prism faces. It is brittle,  $H = 7$ ,  $D_{\text{meas}} = 3.17 \text{ g/cm}^3$ , and  $D_{\text{calc}} = 3.14 \text{ g/cm}^3$ . In plane-polarized light, it is strongly pleochroic, with  $O = \text{pale lavender}$  and  $E = \text{dark blue}$ . Foitite is uniaxial negative, with  $\omega = 1.664(1)$ ,  $\epsilon = 1.642(1)$ . It is hexagonal, with space group  $R3m$ ,  $a = 15.967(2)$ ,  $c = 7.126(1) \text{ \AA}$ ,  $V = 1573.3(4) \text{ \AA}^3$ ,  $Z = 3$ . The strongest ten X-ray diffraction lines in the powder pattern are [ $d$  in ångströms ( $I$ ) ( $hkl$ )] 2.573(100)(501), 3.452(91)(102), 6.338(84)(101), 2.944(71)(212), 4.212(48)(211), 3.989(38)(220), 2.038(29)(512), 1.268(25)(505), 4.964(21)(201), 1.449(18)(650,642,514). Analysis by a combination of electron microprobe and crystal-structure refinement gave  $\text{SiO}_2$  35.90 wt%,  $\text{Al}_2\text{O}_3$  34.90,  $\text{FeO}$  11.45,  $\text{MnO}$  1.71,  $\text{MgO}$  0.21,  $\text{CaO}$  0.03,  $\text{Na}_2\text{O}$  0.75,  $\text{Li}_2\text{O}_{\text{calc}} = 0.31$ ,  $\text{B}_2\text{O}_3_{\text{calc}} = 10.37$ ,  $\text{H}_2\text{O}_{\text{calc}} = 3.56$ , sum = 99.19 wt%, Cu, Ti, F, K not detected. The formula unit (31 anions, with Li sufficient to fill the Y site) is  ${}^x(\square_{0.75}\text{Na}_{0.25}){}^y(\text{Li}_{0.22}\text{Mg}_{0.05}\text{Fe}_{1.60}^{2+}\text{Mn}_{0.24}^{2+}\text{Al}_{0.89}){}^z\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ , with the ideal end-member formula  $\square[\text{Fe}_2^+(\text{Al}, \text{Fe}^{3+})]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ ; thus foitite can be derived from schorl [ $\text{NaFe}_3^+\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_4$ ] by the substitution  ${}^x\square + {}^y\text{Al} \rightarrow {}^x\text{Na} + {}^y\text{Fe}^{2+}$ , where  $\square = \text{vacancy}$ .

The crystal structure of foitite was refined to an  $R$  index of 1.6% using 1128 observed ( $5\sigma$ ) reflections collected with  $\text{MoK}\alpha$  X-radiation. The structure refinement confirmed the low occupancy of the X site and the dominantly divalent state of the Fe at the Y site. There is considerable positional disorder at the O1 and O2 sites induced by the local variations in bond valence distribution with  $\square$ -Na disorder at X and  $\text{Fe}^{2+}$ -Al disorder at Y.

## INTRODUCTION

The general formula of tourmaline may be written as  $XY_3Z_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3W_4$  where  $X = \text{Na, Ca, } \square$ ;  $Y = \text{Mg, Fe}^{2+}, \text{Mn}^{2+}, \text{Al, Fe}^{3+}, \text{Mn}^{3+}, \text{Li}$ ;  $Z = \text{Al, Fe}^{3+}, \text{Cr}^{3+}, \text{Mg}$ ; and  $W = \text{OH, F, O}^{2-}$  and extensive solid solution occurs among a wide variety of end-members. The X site is occupied most commonly by Na but also can incorporate Ca, leading to the end-members liddicoatite, uvite, and feruvite. The extent of these substitutions has been examined by Foit and Rosenberg (1977), Burt (1989), and Henry and Dutrow (1990), among others. The cation occupancy of the X site can also be  $<1$  apfu (atom per formula unit), and such tourmalines are frequently referred to as alkali deficient (Foit et al., 1989).

During a systematic examination of a wide variety of tourmalines, we encountered alkali-deficient tourmaline with substantial vacancy ( $\square$ ) at the X site. This warrants description as a new species, the first of a possible family of alkali- and alkaline-earth-free tourmalines.

Foitite is named for Franklin F. Foit, Jr., (born 1942), Washington State University, Pullman, Washington, in recognition of his work on the structure and chemistry of the tourmaline minerals. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. The type material is preserved at the Canadian Museum of Nature (no. CMN-81512).

## OCCURRENCE

Foitite was found in the mineral collection of the Department of Geology, Dalhousie University, Halifax, Nova Scotia. The locality was given as southern California, and foitite was there as single crystals with no matrix. Tourmaline is a common constituent of a large number of granitic pegmatites in southern California, and it seems reasonable to conclude that foitite was originally collected from such an environment. The composition of foitite would support this conclusion, as alkali depletion is char-

TABLE 1. Chemical analysis and formula unit\* for foitite

SiO <sub>2</sub>	35.90	Si	Si	6.01
Al <sub>2</sub> O <sub>3</sub>	34.90			
FeO	11.45	Z	Al	6.00
MnO	1.71			
MgO	0.21	Y	Fe <sup>2+</sup>	1.60
CaO	0.03		Mn <sup>2+</sup>	0.24
Na <sub>2</sub> O	0.75		Mg	0.05
Li <sub>2</sub> O**	(0.31)		Al	0.89
B <sub>2</sub> O <sub>3</sub> †	(10.37)		Li	0.22
H <sub>2</sub> O‡	(3.56)	Total	Y	3.00
Total	99.19			
		X	Na	0.25
		B	B	3.0
			OH	4.0

\* Calculated assuming 31 anions pfu.

\*\* Calculated to fill the Y site.

† Calculated assuming 3 B apfu.

‡ Calculated assuming 4 H apfu.

acteristic of some pegmatitic environments (Foit and Rosenber, 1977).

### PHYSICAL AND OPTICAL PROPERTIES

Foitite is bluish black, is translucent in thin splinters, and has a vitreous luster; it has a grayish white streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Only two isolated single crystals (~20 × 4 mm) are known. These occur as striated prisms of triangular cross section, terminated by irregular fractures. Foitite has a Mohs hardness of ~7 and no cleavage, and is brittle. The density, measured by hydrostatic weighing in toluene, is 3.17 g/cm<sup>3</sup>, compared with the calculated density of 3.14 g/cm<sup>3</sup>.

TABLE 2. Indexed powder pattern for foitite

<i>hkl</i>	<i>d</i> <sub>calc</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i>
101	6.337	6.338	84
201	4.962	4.964	21
300	4.606	4.607	6
211	4.214	4.212	48
220	3.989	3.989	38
102	3.453	3.452	91
311	3.376	3.375	6
202	3.168	3.166	4
410	3.015	3.014	7
212	2.945	2.944	71
321	2.897	2.896	5
501	2.576	2.573	100
511	2.344	2.344	8
502	2.184	2.185	11
431	2.165	2.165	6
303	2.112	2.112	17
512	2.037	2.038	29
620	1.916	1.917	15
432			
413	1.867	1.867	8
621	1.851	1.851	7
603	1.654	1.655	15
404	1.584	1.584	11
443	1.528	1.527	5
504	1.498	1.499	11
650	1.449	1.449	18
642			
514			
10,1,0	1.311	1.311	5
505	1.267	1.268	25

TABLE 3. Unit-cell dimensions and data pertaining to crystal structure refinement of foitite

<i>a</i> (Å)	15.967 (2)	radiation	MoK $\alpha$
<i>c</i> (Å)	7.126 (1)	scan mode	$\theta$ - $2\theta$
<i>V</i> (Å <sup>3</sup> )	1573.3 (4)	$\theta$ range	2-30°
Sp. gr.	<i>R</i> 3 <i>m</i>	<i>F</i>   <sub>tot</sub>	1128
<i>R</i> <sub>obs</sub>	1.80%	<i>F</i> <sub>obs</sub>	1124
<i>R</i> <sub>int</sub>	3.01%	<i>R</i> <sub>az</sub>	0.93%

In transmitted light, foitite is strongly pleochroic, with *O* = pale lavender, *E* = dark blue. It is uniaxial negative with indices of refraction  $\omega = 1.664(1)$ ,  $\epsilon = 1.642(1)$  measured with gel-filtered Na light ( $\lambda = 589.9$  nm).

### CHEMICAL COMPOSITION

Foitite was analyzed by electron microprobe using a Cameca SX-50 operating in the wavelength-dispersion mode with the following conditions: excitation voltage 15 kV, specimen current 20 nA, peak count time 20 s, background count time 10 s. The following standards and crystals were used for *K* $\alpha$  X-ray lines: Si = diopside, PET; Al = kyanite, TAP; Fe = fayalite, LiF; Mn = spessartine, LiF; Mg = olivine, TAP; Ca = diopside, PET; Na = albite, TAP; in addition, Cu, Ti, K, F were sought but not detected. Data reduction was done using the  $\phi(\rho Z)$  procedure of Pouchou and Pichoir (1985). The crystal used for the optical measurements was analyzed at ten different points. Slight compositional zoning was present; the average analysis is given in Table 1.

Stereochemical and site-scattering results from the crystal structure refinement (see below) show all Fe and Mn to be in the divalent state and show a small amount of Li to be present. Charge-balance requirements also show foitite to be fully protonated. The unit formula was calculated on the basis of 31 anions, with Li<sub>2</sub>O sufficient for full occupancy of the Y site, and B<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O calculated for tourmaline stoichiometry.

### X-RAY CRYSTALLOGRAPHY

The powder-diffraction pattern for a bulk sample was recorded on a Philips PW 1710 diffractometer with graphite-monochromatized CuK $\alpha$  X-radiation. Peak positions were measured by fitting a five-point parabolic curve to the top of the diffraction peaks, followed by correction for  $\alpha_1$ - $\alpha_2$  splitting; NBS Si was used as a standard. Cell dimensions were refined from the corrected *d* values using the program CELREF (Appleman and Evans, 1973); the indexed powder pattern and refined cell dimensions are given in Table 2.

### CRYSTAL STRUCTURE

A fragment of foitite was ground to a sphere and mounted on a Nicolet R3m four-circle diffractometer. Cell dimensions and intensity data were obtained according to the experimental procedure of Hawthorne et al. (1993). Refined unit-cell dimensions and selected data pertaining to crystal-structure refinement are given in Table 3.

TABLE 4. Final parameters for the crystal structure of foitite

Atom	x	y	z	$U_{eq}^*$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
X	0	0	0.84080	267 (28)	282 (36)	282 (36)	237 (47)	0	0	141 (18)
Y	0.06223 (2)	0.93777 (2)	0.4485 (13)	85 (2)	60 (2)	60 (2)	122 (3)	-5 (1)	5 (1)	21 (2)
Z	0.26151 (4)	0.29827 (4)	0.4623 (13)	62 (2)	69 (3)	61 (2)	56 (2)	-3 (2)	-5 (2)	33 (2)
Si	0.18988 (3)	0.19193 (3)	0.0730 (13)	51 (2)	46 (2)	47 (2)	56 (2)	2 (2)	3 (1)	21 (2)
B	0.88981 (11)	0.11019 (11)	0.6177 (14)	86 (7)	88 (8)	88 (8)	73 (10)	2 (4)	-2 (4)	38 (9)
O1	0	0	0.2931 (14)	313 (12)	432 (16)	432 (16)	75 (15)	0	0	216 (8)
O2	0.93776 (7)	0.06224 (7)	0.5853 (14)	197 (8)	303 (10)	303 (10)	121 (9)	-1 (3)	1 (3)	253 (10)
O3	0.13427 (7)	0.86573 (7)	0.5649 (13)	111 (5)	104 (5)	104 (5)	58 (7)	-7 (3)	7 (3)	2 (7)
O4	0.90631 (7)	0.09369 (7)	0.0058 (13)	92 (5)	76 (6)	76 (6)	85 (7)	5 (3)	-5 (3)	8 (6)
O5	0.09452 (7)	0.90548 (7)	-0.0179 (13)	93 (5)	74 (5)	74 (5)	79 (7)	9 (3)	-9 (3)	-2 (6)
O6	0.18786 (9)	0.19831 (9)	0.2977 (13)	77 (4)	85 (5)	76 (6)	50 (5)	-3 (4)	6 (4)	24 (4)
O7	0.28601 (9)	0.28512 (9)	-0.0066 (13)	73 (4)	56 (5)	64 (5)	78 (5)	4 (4)	17 (4)	14 (4)
O8	0.27138 (10)	0.21049 (10)	0.6319 (13)	90 (5)	117 (6)	73 (5)	93 (5)	-8 (4)	-30 (4)	58 (5)

\*  $U_{ij} = U_{ij} \times 10^4$ .

The structure refinement was initiated with the atomic coordinates of dravite (Hawthorne et al., 1993), and rapidly converged to an  $R$  index of  $\sim 1.8\%$  for an anisotropic displacement model. The crystal used in the measurement of the X-ray intensity data was subsequently analyzed by electron microprobe techniques (see above), and the most appropriate X-ray scattering factors were used at the final stages of refinement, which converged to an  $R$  index of 1.6% for 1128 observed ( $5\sigma$ ) reflections. Final atomic parameters are given in Table 4, observed and calculated structure factors are listed in Table 5,<sup>1</sup> selected interatomic distances and angles are given in Table 6, and the refined site-scattering values are given in Table 7. Ionic radii are from Shannon (1976).

## DISCUSSION

### Site-scattering refinement

The refined site-scattering value for the X-site cations (Table 7) is in very close agreement with that expected for the site contents, indicated by the formula unit calculated from the electron microprobe analysis (Table 1). This confirms the low occupancy of the X site by Na, showing that a vacancy is the dominant component at that site.

The refined site-scattering values at the Y and Z sites (Table 7) show occupancy of the Z site by a small amount of scattering species of higher atomic number. Assignment of 0.11 Fe apfu to the Z site brings the effective scattering at both the Y and the Z sites into very close agreement ( $<1\%$ ) with the refined site-scattering values.

### Site populations

The  $\langle Z-O \rangle$  distance of 1.910 Å indicates that the Z site is dominated by Al (Hawthorne et al., 1993). The site-scattering refinement indicates the presence of a small amount of transition metal, but the amount is too small for polyhedral size to be indicative of the valence state.

The  $\langle Y-O \rangle$  distance of 2.044 Å indicates that Fe at this site is (dominantly) in the divalent state (Hawthorne et al., 1993). The final assigned site populations are given in Table 8.

TABLE 6. Selected interatomic distances (Å) and angles (°)

Si-O4a	1.621 (4)	O4a-Si-O5b	106.5 (4)
Si-O5b	1.634 (5)	O4a-Si-O6	111.4 (5)
Si-O6	1.606 (13)	O4a-Si-O7c	109.9 (4)
Si-O7c	1.615 (5)	O5b-Si-O6	110.4 (4)
(Si-O)	1.619	O5b-Si-O7c	109.3 (4)
		O6-Si-O7c	109.4 (4)
		(O-Si-O)	109.4
B-O2	1.346 (1)	O2-B-O8d × 2	120.8 (2)
B-O8a,d	1.391 (2)	O8d-B-O8e	118.4 (2)
(B-O)	1.376	(O-B-O)	120.0
Z-O3e	1.981 (5)	O3e-Z-O6	83.9 (2)
Z-O6	1.852 (8)	O3e-Z-O7g	94.5 (4)
Z-O7f	1.958 (7)	O3e-Z-O8	92.4 (4)
Z-O7g	1.874 (10)	O3e-Z-O8g	95.1 (2)
Z-O8	1.916 (8)	O6-Z-O7f	92.7 (4)
Z-O8g	1.876 (8)	O6-Z-O8	91.0 (3)
(Z-O)	1.910	O6-Z-O8g	94.3 (5)
		O7f-Z-O7g	90.3 (1)
		O7f-Z-O8	96.5 (7)
		O7f-Z-O8g	77.2 (3)
		O7g-Z-O8	78.3 (4)
		O7g-Z-O8g	96.5 (3)
		(O-Z-O)	90.1
Y-O1h	2.047 (7)	O1h-Y-O2i,j	84.3 (2)
Y-O2i,j	1.978 (7)	O1-Y-O6e,k	97.8 (4)
Y-O3	2.158 (5)	O2i-Y-O2j	97.8 (4)
Y-O6e,k	2.051 (7)	O2i,j-Y-O6e,k	87.4 (2)
(Y-O)	2.044	O3-Y-O2i,j	102.3 (4)
		O3-Y-O6e,k	75.0 (2)
		O6e-Y-O6k	87.4 (4)
		(O-Y-O)	90.0
X-O2a,h,l	2.505 (7)	O2a-X-O2h × 3	73.0 (2)
X-O4m,n,o	2.845 (4)	O2a-X-O4m × 6	127.8 (1)
X-O5e,p,q	2.802 (3)	O2a-X-O4o × 3	71.0 (2)
(X-O)	2.717	O2a-X-O5e × 6	86.6 (2)
		O4m-X-O4n × 3	104.1 (2)
		O4m-X-O5e × 6	55.0 (1)
		O4n-X-O5p × 3	134.5 (2)
		O5e-X-O5p × 3	107.8 (2)

Note: equivalent positions are as follows: a =  $-x + y, z$ ; b =  $x, x - y, 1 + z$ ; c =  $x, y, 1 + z$ ; d =  $1 - y, 1 + x - y, z$ ; e =  $x, x - y, z$ ; f =  $1/2 - y, 3/4 + x - y, 3/4 + z$ ; g =  $3/8 - x + y, 1 + 1/2 - x, 1/2 + z$ ; h =  $1 - x + y, 1 - x, z$ ; i =  $1 + x, 1 + x - y, z$ ; j =  $-x + y, -x, z$ ; k =  $1 - x + y, 1 - x, z$ ; l =  $1 + x, 2 + x - y, z$ ; m =  $1 + x, y, -1 + z$ ; n =  $1 + x, 2 + x - y, -1 + z$ ; o =  $-x + y, y, -1 + z$ ; p =  $x, 1 + y, z$ ; q =  $2 - x + y, 1 + y, z$ .

<sup>1</sup> A copy of Table 5 may be ordered as Document AM-93-540 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 7.** Site-scattering values (epfu) in foitite compared with analogous values assigned from the formula unit and the final site populations

Site	X-ray	EMP	Site populations
X	2.9 (1)	2.8	2.8
Y	59.9 (2)	60.4	59.5
Z	79.4 (3)	78.0	79.9

### Anion disorder

The equivalent isotropic displacement factors at the O1 and O2 sites are much larger than those at the other anion positions (Table 4), and the same applies to the X site. This factor has been discussed in some detail by Burns et al. (1994), who attributed this feature in elbaite tourmalines to perturbations associated with different local arrangements of cations coordinating these two anions. A similar argument may be invoked here. The O1 anion is bonded to three Y cations and the O2 anion is bonded to one Y and one X cations; the Y cations may be Al, Fe<sup>2+</sup> (or Li) and the X cations may be Na or □. The wide diversity of bond valence arrangements induces significant positional disorder at these two positions as each anion locally adopts a position that satisfies its bond valence requirements according to the specific local cation configuration to which it is coordinated.

### Ideal formula of foitite

End-member foitite has the ideal formula □[Fe<sub>2</sub><sup>2+</sup>(Al, Fe<sup>3+</sup>)]Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>4</sub>, the most novel characteristic being the vacant X site. Tourmalines of this stoichiometry (i.e., the Mg equivalent of foitite) have been

**TABLE 8.** Site populations (apfu) in foitite

Z	Y	X
5.89 Al	1.00 Al	0.25 Na
0.11 Fe	1.49 Fe <sup>2+</sup>	0.75 □
	0.24 Mn <sup>2+</sup>	
	0.05 Mg	
	0.22 Li	

synthesized by Rosenberg and Foit (1979) and Werding and Schreyer (1984), and the relation of this composition to general tourmaline stoichiometry has been discussed by Burt (1989) and Foit et al., (1989). Foitite can be derived from schorl [NaFe<sub>2</sub><sup>3+</sup>Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>4</sub>] by the substitution <sup>X</sup>□ + <sup>Y</sup>Al → <sup>X</sup>Na + <sup>Y</sup>Fe<sup>2+</sup>, represented by the exchange vector <sup>X</sup>□<sup>Y</sup>Al(<sup>X</sup>Na<sup>Y</sup>Fe<sup>2+</sup>)<sub>-1</sub>, and is only one of a possible family of tourmaline compositions with a vacant X site. These are illustrated in Figure 1 for the general cations M<sup>2+</sup> and M<sup>3+</sup>, assuming that Li is the only monovalent cation to occupy the Y site. As is apparent from Table 1, foitite shows solid solution toward the □(LiM<sub>2</sub><sup>3+</sup>)Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>4</sub> composition. Although we have no evidence for this point, the fact that Li ~ Mn in foitite (Table 1), together with the common association of Li and Mn<sup>3+</sup> in elbaite (e.g., Burns et al., 1994), suggests that Mn may be trivalent in foitite.

### Natural alkali-deficient tourmaline

Foit et al. (1989) have reported alkali-deficient tourmaline compositions within the foitite composition field, occurring in hydrothermally altered tuffs. These cover a considerable range within the foitite compositional field (Foit et al., 1989, their Fig. 4), indicating that compositional variations in these alkali-deficient tourmalines are sensitive to equilibration conditions.

### ACKNOWLEDGMENTS

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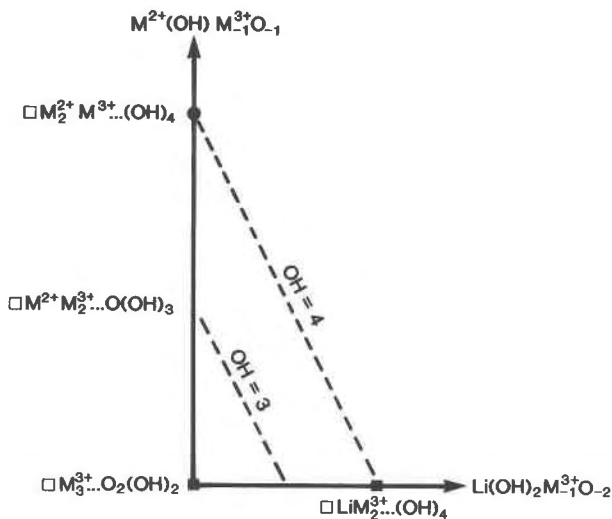


Fig. 1. X-site vacant tourmaline compositions derived from the additive composition  $\square Al_3Al_3Si_6O_{18}(BO_3)_3(OH)_2$  by operation of the exchange vectors  $M^{2+}(OH)M_{-1}^{3+}O_{-1}$  (vertical) and  $Li(OH)_2M_{-1}^{3+}O_{-2}$  (horizontal); the foitite composition is shown by a solid circle.

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