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# FLUOR-DRAVITE, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, A NEW MINERAL SPECIES OF THE TOURMALINE GROUP FROM THE CRABTREE EMERALD MINE, MITCHELL COUNTY, NORTH CAROLINA: DESCRIPTION AND CRYSTAL STRUCTURE

Christine M. CLARK[§] and Frank C. HAWTHORNE[¶]

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

Luisa OTTOLINI

*Istituto di Geoscienze e Georisorse, Unità di Pavia, Consiglio Nazionale delle Ricerche, via A. Ferrata 1, I–27100 Pavia, Italy*

## Abstract

Fluor-dravite, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, is a new mineral species of the tourmaline group from the Crabtree emerald mine, Mitchell County, North Carolina, U.S.A. It occurs as isolated anhedral grains up to a few mm across at or near the boundary of a small body of granitic pegmatite with the surrounding country-rock, and is associated with plagioclase, K-feldspar, quartz, beryl, muscovite, garnet, biotite and fluorite. Crystals are blackish brown with a pale brown streak. Fluor-dravite is brittle and has a Mohs hardness of 7; it is non-fluorescent, has no observable cleavage or parting, and has a calculated density of 3.120 g cm$^{-3}$. In plane-polarized light, it is pleochroic, O = pale yellow-brown, E = colorless. Fluor-dravite is uniaxial negative, $\omega$ = 1.645(2), $\varepsilon$ = 1.621(2). Fluor-dravite is rhombohedral, space group $R3m$, $a$ = 15.955(3), $c$ = 7.153(2) Å, $V$ = 1576.9(6) Å$^3$, $Z$ = 3. The strongest ten X-ray-diffraction lines in the powder pattern [$d$ in Å($I$)($hkl$)] are: 3.475(100)(102), 2.583(67)(051), 2.961(60)(212), 1.920(27)(432), 3.998(22)(220), 6.375(19)(011), 2.043(19)(512), 2.392(14)(003), 2.123(14)(303) and 1.660(14)(063). Analysis by a combination of electron microprobe, SIMS and crystal-structure refinement gives $SiO_2$ 36.02, $Al_2O_3$ 31.69, $TiO_2$ 0.25, FeO 6.41, MnO 0.67, ZnO 0.05, MgO 7.71, CaO 0.25, $Na_2O$ 2.80, $B_2O_{3\ calc}$ 10.86, $Li_2O_{calc}$ 0.20, F 1.45, $H_2O$ 3.19, sum 100.94 wt%. The formula unit is $(Na_{0.88}Ca_{0.04})_{\Sigma 0.92}$ $(Mg_{1.87}Fe_{0.87}Mn_{0.09}Zn_{0.01}Ti_{0.03}Li_{0.13})_{\Sigma 3.00}$ $Al_6$ $(Si_{5.87}B_{0.05}Al_{0.08})$ $O_{18}$ $(BO_3)_3$ $(OH)_3$ $[(OH)_{0.47}F_{0.75})]_{\Sigma 1.22}$. Fluor-dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3$ $(OH)_3F$, is related to end-member dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3(OH)$, by the substitution F → (OH).

*Keywords*: fluor-dravite, tourmaline, new mineral species, electron-microprobe analysis, optical properties, crystal-structure refinement, Crabtree emerald mine, North Carolina, U.S.A.

## Sommaire

La fluor-dravite, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, est une nouvelle espèce minérale du groupe de la tourmaline provenant de la mine d'émeraude de Crabtree, comté de Mitchell, en Caroline du Nord. Elle se présente en grains xénomorphes isolés atteignant quelques mm de taille près du contact d'un petit massif de pegmatite granitique avec l'encaissant. Lui sont associés plagioclase, feldspath potassique, quartz, béryl, muscovite, grenat, biotite et fluorite. Les cristaux sont bruns et noirâtres avec une rayure brun pâle. La fluor-dravite est cassante, avec une dureté de Mohs de 7; elle est non fluorescente, ne possède aucun clivage ou plan de séparation, et sa densité calculée est 3.120 g cm$^{-3}$. En lumière polarisée en plan, elle est pléochroïque, O = jaune-brun pâle, E = incolore. La fluor-dravite est uniaxe négative, $\omega$ = 1.645(2), $\varepsilon$ = 1.621(2). Elle est rhomboédrique, groupe spatial $R3m$, $a$ 15.955(3), $c$ 7.153(2) Å, $V$ 1576.9(6) Å$^3$, $Z$ = 3. Les dix raies du cliché de diffraction X les plus intenses [$d$ en Å($I$)($hkl$)] sont: 3.475(100)(102), 2.583(67)(051), 2.961(60)(212), 1.920(27)(432), 3.998(22)(220), 6.375(19)(011), 2.043(19)(512), 2.392(14)(003), 2.123(14)(303) et 1.660(14)(063). Une analyse effectuée avec une microsonde électronique, une microsonde ionique et un affinement de la structure a donnée $SiO_2$ 36.02, $Al_2O_3$ 31.69, $TiO_2$ 0.25, FeO 6.41, MnO 0.67, ZnO 0.05, MgO 7.71, CaO 0.25, $Na_2O$ 2.80, $B_2O_{3\ calc}$ 10.86, $Li_2O_{calc}$ 0.20, F 1.45, $H_2O$ 3.19, pour un total de 100.94 % (poids). L'unité formulaire est $(Na_{0.88}Ca_{0.04})_{\Sigma 0.92}$ $(Mg_{1.87}Fe_{0.87}Mn_{0.09}Zn_{0.01}Ti_{0.03}Li_{0.13})_{\Sigma 3.00}$ $Al_6$ $(Si_{5.87}B_{0.05}Al_{0.08})$ $O_{18}$ $(BO_3)_3$ $(OH)_3$ $[(OH)_{0.47}F_{0.75})]_{\Sigma 1.22}$. La fluor-dravite, de formule idéale $NaMg_3Al_6Si_6O_{18}(BO_3)_3$ $(OH)_3F$, est liée au pôle dravite, de formule idéale, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3(OH)$, selon la substitution F → (OH).

(Traduit par la Rédaction)

*Mots-clés*: fluor-dravite, tourmaline, nouvelle espèce minérale, données de microsonde électronique, propriétés optiques, affinement de la structure, mine d'émeraude de Crabtree, Caroline du Nord.

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[§] *Current address*: Department of Geography and Geology, Eastern Michigan University, Ypsilanti, Michigan 48197, U.S.A.

[¶] *E-mail address*: frank_hawthorne@umanitoba.ca

## INTRODUCTION

The minerals of the tourmaline supergroup are common phases in a wide variety of rocks, and are of considerable potential use as indicator minerals. We may write the general formula of tourmaline as

$$X\ Y_3\ Z_6\ [T(1)_6O_{18}]\ [T(2)_3O_3]_3\ V_3\ W$$

where $X$ = Na, K, Ca, $Pb^{2+}$, Bi, □ (vacancy), $Y$ = Li, Mg, $Fe^{2+}$, $Mn^{2+}$, Al, $Cr^{3+}$, $V^{3+}$, $Fe^{3+}$, Ti, $Z$ = Mg, $Fe^{2+}$, Al, $Fe^{3+}$, $V^{3+}$, $Cr^{3+}$, $T(1)$ = Si, Al, B, $T(2)$ = B, $V$ = OH, O, $W$ = OH, F, O. The high chemical compliance of the structure allows dominance of many of the above chemical constituents at one or more sites in the structure and gives rise to many distinct mineral species (Hawthorne & Henry 1999, Henry *et al.* 2011).

Systematic work on the crystal chemistry of the tourmaline-group minerals (Clark McCracken 2002) resulted in the discovery of the "fluor-" equivalent of dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$; formal description of the species is given here. The name was assigned for the chemical composition as recommended by Henry *et al.* (2011). The new species and the new name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Classification (IMA 2009–085). The holotype material is deposited in the Smithsonian Institution, catalogue number 121341. We provide here a full characterization of its physical, chemical and structural attributes.

## OCCURRENCE AND PHYSICAL PROPERTIES

Fluor-dravite occurs at the Crabtree emerald mine, Mitchell County, North Carolina, U.S.A. (Schabilion 2009), at the boundary of the pegmatite and the country rock, in association with K-feldspar, plagioclase, quartz, beryl, muscovite, garnet, biotite and fluorite. Fluor-dravite is blackish brown with a vitreous luster. It has a pale-brown streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Crystals are anhedral, up to a few mm across, and occur as isolated grains. Fluor-dravite has a Mohs hardness of 7 and is brittle with a conchoidal fracture; the calculated density is 3.120 g $cm^{-3}$.

A spindle stage was used to orient a crystal for measurement of the indices of refraction. The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, fluor-dravite is pleochroic with O = pale yellow-brown, E = colorless. Fluor-dravite is uniaxial negative with indices of refraction $\omega = 1.645(2)$, $\varepsilon = 1.621(2)$ measured with gel-filtered Na light ($\lambda$ = 589.9 nm).

## CHEMICAL COMPOSITION

Fluor-dravite was analyzed primarily with an electron microprobe using a Cameca SX–100 operating in wavelength-dispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 μm, peak-count time 20 s and background-count time 10 s. The following standards and crystals were used: Si, Ca: diopside, TAP; Ti: titanite, LiF; Fe: fayalite, LiF; Mn: spessartine, LiF; Mg: forsterite, TAP; Na: albite, TAP; Al: kyanite, TAP; F: fluororiebeckite, TAP; Zn: gahnite, LiF. Data reduction was done using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The amount of H was established by SIMS according to the procedure of Ottolini & Hawthorne (2001) and Ottolini *et al.* (2002), and the amount of Li was derived by SREF (see section on crystal-structure refinement). The average result of 10 analyses on a single grain is given in Table 1. The end-member formula of reference is $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, which requires $SiO_2$ 36.35, $Al_2O_3$ 30.84, MgO 12.19, $Na_2O$ 6.25, $B_2O_3$ 10.53, $H_2O$ 2.73, F 1.92, O ≡ F –0.81, total 100.00 wt.%. The chemical formula was calculated on the basis of 31 anions with Li = 9 – (Si + Al + Mg + $Fe^{2+}$ + $Mn^{2+}$ + $Ti^{4+}$ + Zn) *apfu*. The Si value is less than 6 *apfu*, indicating the presence of other cations at the *T* site. The <*T*–O> distance is 1.619 Å, close to the value of 1.620 Å proposed as the <Si–O> distance in the tourmaline structure by MacDonald & Hawthorne (1995). Substitution of Al at the *T* site increases the <*T*–O> distance (MacDonald & Hawthorne 1995) whereas substitution

TABLE 1. CHEMICAL COMPOSITION AND UNIT FORMULA* OF FLUOR-DRAVITE

| | | | |
|---|---|---|---|
| $SiO_2$ wt% | 36.02 | Si *apfu* | 5.86 |
| $TiO_2$ | 0.25 | Al | 0.07 |
| $Al_2O_3$ | 31.69 | B | 0.07 |
| FeO | 6.41 | Sum *T* | 6.00 |
| MnO | 0.67 | | |
| ZnO | 0.05 | $^{Z}$Al | 6.00 |
| MgO | 7.71 | | |
| CaO | 0.25 | $^{Y}$Al | 0.01 |
| $Na_2O$ | 2.80 | $Ti^{4+}$ | 0.03 |
| $Li_2O$ | 0.19 | $Fe^{2+}$ | 0.87 |
| $B_2O_3$ | 10.91 | $Mn^{2+}$ | 0.09 |
| $H_2O$ | 3.19 | Zn | 0.01 |
| F | 1.45 | Mg | 1.87 |
| -O=F | -0.61 | Li | 0.12 |
| | | Sum *Y* | 3.00 |
| Total | 101.00 | | |
| | | Ca | 0.04 |
| | | Na | 0.88 |
| | | Sum *X* | 0.92 |
| | | | |
| | | OH | 3 |
| | | | |
| | | F | 0.75 |
| | | OH | 0.46 |

* Note that the assignment of cations to the *Y* position of the formula follows the usual method of assignment; it does not correspond to the site population of the *Y* site.

of B at the *T* site decreases the <*T*–O> distance (*e.g.*, Hawthorne 1996, Ertl *et al.* 2006, 2007, Lussier *et al.* 2008). Also, it has been confirmed directly that all three cations can occupy (long range) the *T* site simultaneously (Lussier *et al.* 2009). Consequently, we adjusted the $B_2O_3$ content during the normalization procedure until $^{[4]}$Al ≈ $^{[4]}$B. The resulting chemical formula is given in Table 1.

## X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded from a small fragment on a Gandolfi camera with Fe-filtered Cu*K*α X-radiation. Unit-cell dimensions were refined from the corrected *d* values; the indexed powder pattern and refined unit-cell dimensions are given in Table 2. Peak intensities reported in Table 2 are those estimated by eye from the degree of darkening of the film.

## CRYSTAL-STRUCTURE REFINEMENT AND CRYSTAL CHEMISTRY

Intensity data were collected on a Siemens *P*3 single-crystal diffractometer with a serial detector using graphite-monochromated Mo*K*a X-radiation. The cell parameters (Table 3) and orientation matrix were derived by least-squares refinement of the setting angles of 15 centered reflections. A single asymmetric unit of intensity data was collected (4 → 60° 2θ; θ–2θ scan mode, *hkl* from 0 0 –11 to 23 23 11). A standard reflection was collected every 50 measurements to monitor instrument stability. A second dataset was collected in order to apply a psi-scan empirical absorption correction. The intensities of 15 strong reflections, uniformly distributed with regard to 2θ, were measured over 10° intervals of Ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector from 0 → 360° Ψ), and then used to apply an absorption correction that reduced *R*(azimuthal) from 1.4 to 1.0% for the Ψ-scan data. Intensities were corrected for Lorentz and polarization effects, and reflections with $I > 4\sigma I$ are considered as observed.

The Siemens SHELXTL (PC Version) system of programs was used for unweighted full-matrix least-squares refinement on $|F|$ using neutral scattering factors and anomalous-dispersion corrections. The structure was refined in the space group *R*3*m* with anisotropic-displacement parameters for all atoms, variable site-occupancies for the *X* (Na), *Y* (Mg + Fe) and *W* (O + F) sites, and fixed occupancies for the *Z* (Al), *T* (Si), *B* (B) and all divalent-anion sites (O). The refinement converged to a final $R_1$ index of 1.6%, with maximum positive and negative densities in the final difference-Fourier map of ±0.6 *e*/Å$^3$ and all intervariable correlations less than 0.68. Final parameters of the atoms are given in Table 4, selected interatomic distances in Table 5, and refined site-scattering values (expressed in *epfu*: electrons per formula unit, for the reasons discussed by Hawthorne *et al.* 1995) are given in Table 6. A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Fluor-dravite CM49_57].

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR FLUOR-DRAVITE

| $I_{obs}$ | $d_{obs}$ Å | $d_{calc}$ Å | *h k l* | $I_{obs}$ | $d_{obs}$ Å | $d_{calc}$ Å | *h k l* |
|---|---|---|---|---|---|---|---|
| 19 | 6.375 | 6.368 | 0 1 1 | 27 | 1.920 | 1.921 | 4 3 2 |
| 12 | 4.985 | 4.979 | 2 0 1 | 2 | 1.906 | 1.906 | 3 5 1 |
| 6 | 4.620 | 4.612 | 3 0 0 | 6 | 1.874 | 1.874 | 1 4 3 |
| 22 | 3.998 | 3.994 | 2 2 0 | 3 | 1.853 | 1.854 | 6 2 1 |
| 100 | 3.475 | 3.471 | 1 0 2 | 6 | 1.779 | 1.779 | 3 3 3 |
| 8 | 3.386 | 3.384 | 1 3 1 | 4 | 1.735 | 1.736 | 0 2 4 |
| 4 | 3.023 | 3.020 | 1 4 0 | 14 | 1.660 | 1.660 | 0 6 3 |
| 60 | 2.961 | 2.958 | 2 1 2 | 5 | 1.646 | 1.645 | 7 2 1 |
| 4 | 2.904 | 2.903 | 3 2 1 | 6 | 1.598 | 1.598 | 5 5 0 |
| 4 | 2.621 | 2.620 | 3 1 2 | 4 | 1.592 | 1.592 | 0 4 4 |
| 67 | 2.583 | 2.582 | 0 5 1 | 2 | 1.561 | 1.561 | 3 2 4 |
| 3 | 2.491 | 2.490 | 4 0 2 | 2 | 1.538 | 1.538 | 9 0 0 |
| 14 | 2.392 | 2.391 | 0 0 3 | 3 | 1.529 | 1.529 | 2 7 2 |
| 10 | 2.378 | 2.377 | 3 2 2 | 12 | 1.505 | 1.505 | 5 0 4 |
| 8 | 2.350 | 2.348 | 5 1 1 | 3 | 1.427 | 1.427 | 1 0 5 |
| 7 | 2.191 | 3.191 | 5 0 2 | 3 | 1.422 | 1.422 | 5 6 1 |
| 7 | 2.169 | 2.168 | 3 4 1 | 7 | 1.358 | 1.359 | 0 10 1 |
| 14 | 2.123 | 2.123 | 3 0 3 | 5 | 1.328 | 1.328 | 3 5 4 |
| 6 | 2.114 | 2.113 | 2 4 2 | 2 | 1.325 | 1.325 | 5 7 0 |
| 13 | 2.051 | 2.051 | 2 2 3 | 4 | 1.314 | 1.313 | 10 1 0 |
| 19 | 2.043 | 2.043 | 5 1 2 | 2 | 1.308 | 1.308 | 3 8 2 |
| 7 | 2.025 | 2.024 | 6 1 1 | 5 | 1.274 | 1.274 | 5 0 5 |

Cu*K*α (Ni-filtered) radiation, λ = 1.5406 Å; data for intensities > 2%; outlier rejected data (2σ) not listed; calculated powder-pattern from single-crystal structure. The refinement was used to aid indexing; no internal standard; *a* = 15.978(1), *c* = 7.172(1) Å, *V* = 1585.6(4) Å$^3$.

## DISCUSSION

Bosi & Lucchesi (2007) noted that the difference between the sizes of the *Y* and *Z* octahedra, <*Y*–O> and <*Z*–O>, cannot be too large as it is constrained by the cooperative nature of the tetrahedron rotations that displace the linking O(7) anion as the sizes of the tetrahedra vary. In order to keep this difference small, compositional change that tends to increase the difference in size between the *Y* and *Z* octahedra is accompanied by the disordering reaction $^{Y}Al + {}^{Z}M^{2+} \rightarrow {}^{Y}M^{2+} + {}^{Z}Al$, which will reduce <*Y*–O> and increase <*Z*–O>, thereby reducing the difference in size of the *Y* and *Z* octahedra. Where the cations involved are Mg and Al, the effects of this reaction are not apparent in

TABLE 3. MISCELLANEOUS INFORMATION FOR FLUOR-DRAVITE

| | | | |
|---|---|---|---|
| *a* (Å) | 15.955(3) | crystal size (μm) | 230, sphere |
| *c* | 7.153(2) | radiation/monochromater | Mo*K*α/Graphite |
| *V* (Å$^3$) | 1576.9(6) | No. unique reflections | 1139 |
| | | No. $I_o > 3\sigma I$ | 1137 |
| Space group | *R*3*m* | $R_{az}$ % | 1.4 → 1.0 |
| Z | 3 | $R_{obs}$ % | 1.6 |
| $D_{calc}$ (g cm$^{-3}$) | 3.120 | $R_{all}$ % | 2.6 |
| | | GOF | 2.69 |

TABLE 4. LA–ICP–MS DATA PERTAINING TO REPRESENTATIVE SAMPLES OF TOURMALINE

| | d.l. | Lav–7 | VM–1 | Poz5267 | Koz3–11 | Klu–10 | KluI–3 |
|---|---|---|---|---|---|---|---|
| Li ppm | 24 | 95.1 - 252 | b.d.l. | 90.0 - 359 | b.d.l. | b.d.l. | b.d.l. - 503 |
| Be | 0.5 | 0.6 - 2.0 | 10.8 - 30.9 | 4.6 - 10.1 | 6.0 - 19.0 | 18.7 - 31.5 | 7.0 - 15.0 |
| Sc | 2 | 64.0 - 121 | 34.0 - 135 | 30.2 - 44.1 | 36.2 - 59.7 | 72.0 - 110 | 68.4 - 293 |
| V | 2 | b.d.l. - 6.8 | 94.7 - 219 | 132 - 210 | 41.2 - 75.1 | 42.7 - 70.2 | b.d.l. |
| Ni | 8 | 428 - 754 | 558 - 796 | 356 - 555 | 384 - 598 | 428 - 614 | 726 - 1189 |
| Co | 1 | 5.2 - 8.4 | 1.6 - 21.1 | 1.6 - 2.5 | 8.0 - 12.5 | b.d.l. | b.d.l. |
| Zn | 4 | 5.2 - 684 | b.d.l. - 221 | 63.4 - 188 | 8.0 - 202 | 153 - 264 | 873 - 1440 |
| Ga | 2 | 86.6 - 128 | 54.5 - 116 | 66.2 - 90.7 | 56.9 - 84.1 | 71.0 - 120 | 146 - 184 |
| Sr | 2 | b.d.l. - 6.5 | 93.2 - 136 | 245 - 371 | 206 - 293 | 88.6 - 149 | b.d.l. |
| Nb | 2 | b.d.l. - 2.4 | 6.1 - 20.6 | 5.8 - 8.2 | 3.6 - 8.9 | 7.8 - 11.6 | b.d.l. - 16.3 |
| Sn | 2 | 21.6 - 114 | 597 - 1643 | 1548 - 2109 | 523 - 892 | 818 - 985 | 49.6 - 620 |
| La | 1 | b.d.l. | 26.8 - 51.2 | 10.7 - 14.2 | 12.5 - 27.4 | 22.4 - 35.2 | 6.2 - 37.1 |
| Ce | 1 | b.d.l. | 24.6 - 46.4 | 15.3 - 21.4 | 20.5 - 36.1 | 27.9 - 39.7 | 7.6 - 62.7 |
| Ta | 2 | b.d.l. | b.d.l. - 9.6 | 2.8 - 4.6 | b.d.l. - 4.7 | 2.5 - 3.9 | b.d.l. - 10.0 |
| Pb | 1 | b.d.l. - 5.2 | 24.2 - 44.3 | 50.3 - 78.8 | 30.0 - 68.6 | 24.8 - 55.2 | 21.3 - 72.2 |

d.l.: detection limit; b.d.l.: below the detection limit.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) FOR FLUOR-DRAVITE

| | | | | | |
|---|---|---|---|---|---|
| *X*–O(2) | × 3 | 2.471(2) | *Y*–O(1) | | 2.061(2) |
| *X*–O(4) | × 3 | 2.813(1) | *Y*–O(2) | × 2 | 2.014(2) |
| *X*–O(5) | × 3 | 2.747(1) | *Y*–O(3) | | 2.146(1) |
| <*X*–O> | | 2.677 | *Y*–O(6) | × 2 | 2.041(2) |
| | | | <*Y*–O> | | 2.053 |
| *Z*–O(3) | | 1.977(2) | | | |
| *Z*–O(6) | | 1.858(2) | *T*–O(4) | | 1.625(1) |
| *Z*–O(7) | | 1.958(2) | *T*–O(5) | | 1.639(2) |
| *Z*–O(7) | | 1.886(3) | *T*–O(6) | | 1.601(3) |
| *Z*–O(8) | | 1.921(3) | *T*–O(7) | | 1.610(2) |
| *Z*–O(8) | | 1.878(2) | <*T*–O> | | 1.619 |
| <*Z*–O> | | 1.913 | | | |
| *B*–O(2) | | 1.351(2) | | | |
| *B*–O(8) | × 2 | 1.388(2) | | | |
| <*B*–O> | | 1.376 | | | |

TABLE 6. REFINED SITE-SCATTERING VALUES (SREF; *epfu*), ASSIGNED SITE-POPULATIONS (*apfu*) AND EQUIVALENT SITE-SCATTERING VALUES (EMPA; *epfu*) FOR FLUOR-DRAVITE

| | SREF | Site population | EMPA |
|---|---|---|---|
| *X* | 10.7(1) | 0.88 Na + 0.04 Ca | 10.5 |
| *Y* | 49.3(3) | 1.30 Mg + 0.87 Fe + 0.58 Al + 0.09 Mn + 0.03 Ti + 0.13 Li | 49.1 |
| *Z* | 78 | 5.43 Al + 0.57 Mg | 77.4 |
| *W* * | 9.3(3) | 0.61 F + 0.39 OH | 8.8 |

* The sum F + (OH) is normalized to 1.0 *apfu*.

the site-scattering values at these two sites. However, the sizes of these two cations are significantly different (Mg = 0.72, Al = 0.535 Å; Shannon 1976), and hence this difference is apparent in the <*Y*–O> and <*Z*–O> distances. This effect was first noticed by Hawthorne *et al.* (1993), and Taylor *et al.* (1995) and Hawthorne (1996, 2002) showed that such disorder may couple to the incorporation of O$^{2–}$ at the *W* position of the chemical formula [the O(1) site in the structure], depending on the details of the local order of cations around the O(1) site. Bosi & Lucchesi (2004) showed that there is considerable $^{Y}\mathrm{Al} + {}^{Z}M^{2+} \rightarrow {}^{Y}M^{2+} + {}^{Z}\mathrm{Al}$ disorder in tourmalines of the schorl–dravite series. Extrapolation of their relations for $^{Z}$Al and $^{Z}$Mg *versus* <*Z*–O> gives <Z–O> values of 1.908 and 1.902 Å, respectively, for $^{Z}\mathrm{Al} = 6$ and $^{Z}\mathrm{Mg} = 0$ *apfu*. The <*Z*–O> value for fluor-dravite is 1.913 Å, significantly greater than the ideal value for $^{Z}\mathrm{Al} = 6$ *apfu*, indicating that there is significant $^{Y}\mathrm{Al} + {}^{Z}M^{2+} \rightarrow {}^{Y}M^{2+} + {}^{Z}\mathrm{Al}$ disorder in this tourmaline. Table 7 shows the bond valences calculated for the ordered model derived from the formula of Table 1 and the bond lengths of Table 5. Inspection of the incident bond-valence sums around the cations shows close-to-ideal values for all sites except *Y*, for which there is significant deviation from the valence-sum rule if all $^{[6]}$Al is assigned to the *Z* site. This result also indicates that there is significant Al at the *Y* site.

Bosi & Lucchesi (2004) provided plots of the relations between <*Z*–O> and both $^{Z}$Al and $^{Z}M$ in tourmalines of the schorl–dravite series. We may use these curves, together with the observed <*Z*–O> distance in fluor-dravite, to derive the amount of Al at the *Z* site and by difference the amount of Al at the *Y* site. In fluor-dravite, <*Z*–O> is equal to 1.913 Å; however, the curves of Bosi & Lucchesi (2004) were derived for tourmalines in which the F content at the *W* position is low (<F> < 0.1 *apfu*), whereas in fluor-dravite, the F content of the W position is high. Thus we must correct the <*Z*–O> distance for fluor-dravite for the high content of F in the tourmaline. The radii of [3]-coordinated (OH) and F are 1.34 and 1.30 Å, respectively (Ribbe & Gibbs 1971, Shannon 1976), there are two O(1) sites in the coordi-

TABLE 7. BOND-VALENCE (*vu*)* TABLE FOR ORDERED FLUOR-DRAVITE

| | *X* | *Y* | *Z* | *T* | *B* | Σ |
|---|---|---|---|---|---|---|
| O(1) | | 0.304 $^{\times3}\rightarrow$ | | | | 0.912 |
| O(2) | 0.158 $^{\times2}\downarrow$ | 0.431 $^{\times2}\downarrow$ | | | 1.056 | 2.076 |
| O(3) | | 0.302 | 0.414 | | | 1.130 |
| O(4) | 0.061 $^{\times2}\rightarrow$ | | | 0.944 $^{\times2}\rightarrow$ | | 2.010 |
| O(5) | 0.074 | | | 0.957 $^{\times2}\rightarrow$ | | 1.988 |
| O(6) | | 0.401 $^{\times2}\downarrow$ | 0.572 | 1.061 | | 2.034 |
| O(7) | | | 0.436<br>0.530 | 1.035 | | 2.001 |
| O(8) | | | 0.482<br>0.541 | | 0.955 $^{\times2}\downarrow$ | 1.978 |
| Σ | 0.879 | 2.270 | 2.975 | 3.997 | 2.966 | |

* Calculated from the curves of Brown & Altermatt (1985).

nation polyhedron of the *Z* site, the adjusted <*Z*–O> distance for fluor-dravite is 1.921 Å, and the resulting amount of $^{Z}$Al is 5.43 *apfu*. Final site-populations are given in Table 6. Inspection of Table 7 shows that the incident bond-valence sum at the *Z* cation is 2.98 *vu* for the ordered model. Calculation of the bond valence incident at *Z* using the disordered site-population of Table 6 gives a value of 2.92 *vu*, close to the formal charge at the Z site: $(5.43 \times 3 + 0.57 \times 2)/6 = 2.91^{+}$, in accord with the valence-sum rule.

The name fluor-dravite is assigned in accord with the recommendations of Henry *et al.* (2011). Fluor-dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, may be derived from the root composition of dravite, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3(OH)$, *via* the homovalent substitution F → (OH) at the *W* position of the ideal formula $X\ Y_3\ Z_6\ T_6\ O_{18}\ (BO_3)_3\ V_3\ W$ (Hawthorne & Henry 1999) and the O(1) site of the crystal structure.

## ACKNOWLEDGEMENTS

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# FLUOR-DRAVITE, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, A NEW MINERAL SPECIES OF THE TOURMALINE GROUP FROM THE CRABTREE EMERALD MINE, MITCHELL COUNTY, NORTH CAROLINA: DESCRIPTION AND CRYSTAL STRUCTURE

CHRISTINE M. CLARK* AND FRANK C. HAWTHORNE

*Department of Geological Sciences, University of Manitoba*

*Winnipeg, MB, R3T 2N2*, *Canada*

LUISA OTTOLINI

*Istituto di Geoscienze e Georisorse, Unità di Pavia, Consiglio Nazionale delle Ricerche,*

*via A. Ferrata 1, I-27100 Pavia*, Italy

* Current address: Department of Geography and Geology, Eastern Michigan University,
Ypsilanti, MI 48197, U.S.A.

# ABSTRACT

Fluor-dravite, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, is a new mineral species of the tourmaline group from the Crabtree emerald mine, Mitchell County, North Carolina, U.S.A. It occurs as isolated anhedral grains up to a few mm across at or near the boundary of a small body of granitic pegmatite with the surrounding country-rock, and is associated with plagioclase, K-feldspar, quartz, beryl, muscovite, garnet, biotite and fluorite. Crystals are blackish brown with a pale brown streak. Fluor-dravite is brittle and has a Mohs hardness of 7; it is non-fluorescent, has no observable cleavage or parting, and has a calculated density of 3.120 g $cm^{-3}$. In plane-polarized light, it is pleochroic, O = pale yellow-brown, E = colourless. Fluor-dravite is uniaxial negative, $\omega = 1.645(2)$, $\varepsilon = 1.621(2)$. Fluor-dravite is rhombohedral, space group $R3m$, $a = 15.955(3)$, $c = 7.153(2)$ Å, $V = 1576.9(6)$ $Å^3$, $Z = 3$. The strongest ten X-ray diffraction lines in the powder pattern are [d in Å(*I*)(*hkl*)]: 3.475(100)(102), 2.583(67)(051), 2.961(60)(212), 1.920(27)(432), 3.998(22)(220), 6.375(19)(011), 2.043(19)(512), 2.392(14)(003), 2.123(14)(303) and 1.660(14)(063). Analysis by a combination of electron microprobe, SIMS and crystal-structure refinement gives $SiO_2$ 36.02, $Al_2O_3$ 31.69, $TiO_2$ 0.25, FeO 6.41, MnO 0.67, ZnO 0.05, MgO 7.71, CaO 0.25, $Na_2O$ 2.80, $B_2O_{3\ calc}$ 10.86, $Li_2O_{calc}$ 0.20, F 1.45, $H_2O$ 3.19, sum 100.94 wt%. The formula unit is $(Na_{0.88}Ca_{0.04})_{\Sigma=0.92}$ $(Mg_{1.87}Fe_{0.87}Mn_{0.09}Zn_{0.01}Ti_{0.03}Li_{0.13})_{\Sigma=3.00}$ $Al_6$ $(Si_{5.87}B_{0.05}Al_{0.08})$ $O_{18}$ $(BO_3)_3$ $(OH)_3$ $[(OH)_{0.47}F_{0.75})]_{\Sigma=1.22}$. Fluor-dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, is related to end-member dravite, ideally, $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3(OH)$ by the substitution F → (OH).

*Keywords*: fluor-dravite, tourmaline, new mineral, electron-microprobe analysis, optical properties, crystal-structure refinement, Crabtree emerald mine, North Carolina, U.S.A.

## INTRODUCTION

The minerals of the tourmaline supergroup are common phases in a wide variety of rocks, and are of considerable potential use as indicator minerals. We may write the general formula of tourmaline as

$$X\ Y_3\ Z_6\ [T(1)_6O_{18}]\ [T(2)_3O_3]_3\ V_3\ W$$

where X = Na, K, Ca, $Pb^{2+}$, Bi, G (vacancy)
Y = Li, Mg, $Fe^{2+}$, $Mn^{2+}$, Al, $Cr^{3+}$, $V^{3+}$, $Fe^{3+}$, Ti
Z = Mg, $Fe^{2+}$, Al, $Fe^{3+}$, $V^{3+}$, $Cr^{3+}$
T(1) = Si, Al, B
T(2) = B
V = OH, O
W = OH, F, O.

The high chemical compliance of the structure allows dominance of many of the above chemical constituents at one or more sites in the structure and gives rise to many distinct mineral species (Hawthorne & Henry 1999, Henry *et al*. 2011).

Systematic work on the crystal chemistry of the tourmaline-group minerals (Clark McCracken 2002) resulted in the discovery of the “fluor-“ equivalent of dravite, ideally $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$; formal description of the species is given here. The name was assigned for the chemical composition as recommended by Henry *et al*. (2011). The new species and the new name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Classification (IMA 2009-085). The holotype material is deposited in the Smithsonian Institution, catalogue number 121341.

## OCCURRENCE AND PHYSICAL PROPERTIES

Fluor-dravite occurs at the Crabtree emerald mine, Mitchell County, North Carolina, U.S.A. (Schabilion 2009) at the boundary of the pegmatite and the country rock, in association with K-feldspar, plagioclase, quartz, beryl, muscovite, garnet, biotite and fluorite. Fluor-dravite is blackish brown with a vitreous luster. It has a pale-brown streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Crystals are anhedral, up to a few mm across, and occur as isolated grains. Fluor-dravite has a Mohs hardness of 7 and is brittle with a conchoidal fracture; the calculated density is 3.120 g $cm^{-3}$.

A spindle stage was used to orient a crystal for measurement of the indices of refraction. The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, fluor-dravite is pleochroic with O = pale yellow-brown, E = colourless. Fluor-dravite is uniaxial negative with indices of refraction $\omega$ = 1.645(2), $\varepsilon$ = 1.621(2) measured with gel-filtered Na light ($\lambda$ = 589.9 nm).

## CHEMICAL COMPOSITION

Fluor-dravite was analyzed primarily with an electron microprobe using a Cameca SX-100 operating in wavelength-dispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 μm, peak-count time 20 s and background-count time 10 s. The following standards and crystals were used: Si, Ca: diopside, TAP; Ti: titanite, LiF; Fe: fayalite, LiF; Mn: spessartine, LiF; Mg: forsterite, TAP; Na: albite, TAP; Al: kyanite, TAP; F: fluororiebeckite, TAP; Zn: gahnite, LiF. Data reduction was done using the $\varphi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The amount of H was established by SIMS according to the procedure of Ottolini *et al*. (2001, 2002) and the amount of Li was derived by SREF (see section on crystal-structure refinement). The average result of 10 analyses on a single grain is given in Table 1. The end-member formula of reference is $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3F$, which requires $SiO_2$ 36.35, $Al_2O_3$ 30.84, MgO 12.19, $Na_2O$ 6.25, $B_2O_3$ 10.53, $H_2O$ 2.73, F 1.92, O ≡ F -0.81, total 100.00 wt.%. The chemical formula was calculated on the basis of 31 anions with Li = 9 – (Si + Al + Mg + $Fe^{2+}$ + $Mn^{2+}$ + $Ti^{4+}$ + Zn) *apfu*. The Si value is less than 6 *apfu*, indicating the presence of other cations at the *T* site. The <*T*-O> distance is 1.619 Å, close to the value of 1.620 Å proposed as the <Si-O> distance in the tourmaline structure by MacDonald & Hawthorne (1995). Substitution of Al at the *T* site increases the <*T*-O> distance (MacDonald & Hawthorne 1995) whereas substitution of B at the *T* site decreases the <*T*-O> distance (*e.g.*, Hawthorne (1996), Ertl *et al*. 2006, 2007, Lussier *et al.* 2008). Also, it has been confirmed directly that all three cations can occupy (long range) the *T* site simultaneously (Lussier *et al.* 2009). Consequently, we adjusted the $B_2O_3$ content during the normalization procedure until $^{[4]}$Al ≈ $^{[4]}$B. The resulting chemical formula is given in Table 1.

## X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded from a small fragment on a Gandolfi camera with Fe-filtered Cu*K*α X-radiation. Unit-cell dimensions were refined from the corrected *d* values; the indexed powder pattern and refined unit-cell dimensions are given in Table 2. Peak intensities reported in Table 2 are those estimated by eye from the degree of darkening of the film.

## CRYSTAL-STRUCTURE REFINEMENT AND CRYSTAL CHEMISTRY

Intensity data were collected on a Siemens *P*3 single-crystal diffractometer with a serial detector using graphite-monochromated Mo*K*α X-radiation. The cell parameters (Table 3) and orientation matrix were derived by least-squares refinement of the setting angles of 15 centered reflections. A single asymmetric unit of intensity data was collected (4 → 60° 2θ; θ–2θ scan mode, *hkl* from 0 0 –11 to 23 23 11). A standard reflection was collected every 50 measurements to monitor instrument stability. A second data-set was collected in order to apply a psi-scan empirical absorption correction. The intensities of 15 strong reflections, uniformly distributed with regard to 2θ, were measured over 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector from 0 → 360° ψ), and then used to apply an absorption correction that reduced $R$(azimuthal) from 1.4 to 1.0% for the ψ-scan data. Intensities were corrected for Lorentz and polarization effects, and reflections with $I > 4\sigma I$ are considered as observed.

The Siemens SHELXTL (PC Version) system of programs was used for unweighted full-matrix least-squares refinement on $|F|$ using neutral scattering factors and anomalous-dispersion corrections. The structure was refined in the space group $R3m$ with anisotropic-displacement parameters for all atoms, variable site-occupancies for the *X* (Na), *Y* (Mg + Fe) and *W* (O + F) sites, and fixed occupancies for the *Z* (Al), *T* (Si), *B* (B) and all divalent-anion sites (O). The refinement converged to a final $R_1$ index of 1.6%, with maximum positive and negative densities in the final difference-Fourier map of ±0.6 e/Å$^3$ and all intervariable correlations less than 0.68. Final atom parameters are given in Table 4, selected interatomic distances in Table 5, and refined site-scattering values (expressed in *epfu*: electrons per formula unit, for the reasons discussed by Hawthorne *et al.* 1995) are given in Table 6. A table of structure factors is available from the Depository of Unpublished Data, MAC website, document CMXX_XXXX.

## DISCUSSION

Bosi & Lucchesi (2007) noted that the difference between the sizes of the *Y* and *Z* octahedra, <*Y*-O> and <*Z*-O>, cannot be too large as it is constrained by the cooperative nature of the tetrahedron rotations that displace the linking O(7) anion as the sizes of the tetrahedra vary. In order to keep this difference small, compositional change that tends to increase the difference in size between the *Y* and *Z* octahedra is accompanied by the disordering reaction $^{Y}\text{Al} + {}^{Z}\text{M}^{2+} \rightarrow {}^{Y}\text{M}^{2+} + {}^{Z}\text{Al}$, which will reduce <*Y*-O> and increase <*Z*-O>, thereby reducing the difference in size of the *Y* and *Z* octahedral. Where the cations involved are Mg and Al, the effects of this reaction are not apparent in the site-scattering values at these two sites. However, the sizes of these two cations are significantly different (Mg = 0.72, Al = 0.535 Å; Shannon

1976) and hence this difference is apparent in the <$Y$-O> and <$Z$-O> distances. This effect was first noticed by Hawthorne *et al*. (1993), and Taylor *et al*. (1995) and Hawthorne (1996, 2002) showed that it such disorder may couple to the incorporation of $O^{2-}$ at the W position of the chemical formula [the O(1) site in the structure], depending on the details of the local order of cations around the O(1) site. Bosi & Lucchesi (2004) show that there is considerable ${}^{Y}Al + {}^{Z}M^{2+} \rightarrow {}^{Y}M^{2+} + {}^{Z}Al$ disorder in tourmalines of the schorl-dravite series. Extrapolation of their relations for ${}^{Z}Al$ and ${}^{Z}Mg$ versus <$Z$-O> gives <Z-O> values of 1.908 and 1.902 Å, respectively, for ${}^{Z}Al = 6$ and ${}^{Z}Mg = 0$ *apfu*. The <$Z$-O> value for fluor-dravite is 1.913 Å, significantly greater than the ideal value for ${}^{Z}Al = 6$ *apfu*, indicating that there is significant ${}^{Y}Al + {}^{Z}M^{2+} \rightarrow {}^{Y}M^{2+} + {}^{Z}Al$ disorder in this tourmaline. Table 7 shows the bond valences calculated for the ordered model derived from the formula of Table 1 and the bond lengths of Table 5. Inspection of the incident bond-valence sums around the cations shows close-to-ideal values for all sites except *Y*, for which there is significant deviation from the valence-sum rule if all ${}^{[6]}Al$ is assigned to the *Z* site. This result also indicates that there is significant Al at the *Y* site.

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### TABLE 1. CHEMICAL COMPOSITION (wt%) AND UNIT FORMULA (*apfu*)* FOR FLUOR-DRAVITE

| | | | |
|---|---|---|---|
| $SiO_2$ | 36.02 | Si | 5.86 |
| $TiO_2$ | 0.25 | Al | 0.07 |
| $Al_2O_3$ | 31.69 | B | 0.07 |
| FeO | 6.41 | Sum T | 6.00 |
| MnO | 0.67 | | |
| ZnO | 0.05 | $^{Z}Al$ | 6.00 |
| MgO | 7.71 | | |
| CaO | 0.25 | $^{Y}Al$ | 0.01 |
| $Na_2O$ | 2.80 | $Ti^{4+}$ | 0.03 |
| $Li_2O$ | 0.19 | $Fe^{2+}$ | 0.87 |
| $B_2O_3$ | 10.91 | $Mn^{2+}$ | 0.09 |
| $H_2O$ | 3.19 | Zn | 0.01 |
| F | 1.45 | Mg | 1.87 |
| -O=F | -0.61 | Li | 0.12 |
| Total | 101.00 | Sum Y | 3.00 |
| | | Ca | 0.04 |
| | | Na | 0.88 |
| | | Sum X | 0.92 |
| | | OH | 3 |
| | | F | 0.75 |
| | | OH | 0.46 |

*Note that the assignment of cations to the Y position of the formula follows the usual method of assignment; it does not correspond to the site population of the *Y* site.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR FLUOR-DRAVITE

| $I_{obs}$ | $d_{(obs.)}$ Å | $d_{(calc)}$ Å | *h k l* | $I_{obs}$ | $d_{(obs)}$ Å | $d_{(calc)}$ Å | *h k l* |
|---|---|---|---|---|---|---|---|
| 19 | 6.375 | 6.368 | 0 1 1 | 27 | 1.920 | 1.921 | 4 3 2 |
| 12 | 4.985 | 4.979 | 2 0 1 | 2 | 1.906 | 1.906 | 3 5 1 |
| 6 | 4.620 | 4.612 | 3 0 0 | 6 | 1.874 | 1.874 | 1 4 3 |
| 22 | 3.998 | 3.994 | 2 2 0 | 3 | 1.853 | 1.854 | 6 2 1 |
| 100 | 3.475 | 3.471 | 1 0 2 | 6 | 1.779 | 1.779 | 3 3 3 |
| 8 | 3.386 | 3.384 | 1 3 1 | 4 | 1.735 | 1.736 | 0 2 4 |
| 4 | 3.023 | 3.020 | 1 4 0 | 14 | 1.660 | 1.660 | 0 6 3 |
| 60 | 2.961 | 2.958 | 2 1 2 | 5 | 1.646 | 1.645 | 7 2 1 |
| 4 | 2.904 | 2.903 | 3 2 1 | 6 | 1.598 | 1.598 | 5 5 0 |
| 4 | 2.621 | 2.620 | 3 1 2 | 4 | 1.592 | 1.592 | 0 4 4 |
| 67 | 2.583 | 2.582 | 0 5 1 | 2 | 1.561 | 1.561 | 3 2 4 |
| 3 | 2.491 | 2.490 | 4 0 2 | 2 | 1.538 | 1.538 | 9 0 0 |
| 14 | 2.392 | 2.391 | 0 0 3 | 3 | 1.529 | 1.529 | 2 7 2 |
| 10 | 2.378 | 2.377 | 3 2 2 | 12 | 1.505 | 1.505 | 5 0 4 |
| 8 | 2.350 | 2.348 | 5 1 1 | 3 | 1.427 | 1.427 | 1 0 5 |
| 7 | 2.191 | 3.191 | 5 0 2 | 3 | 1.422 | 1.422 | 5 6 1 |
| 7 | 2.169 | 2.168 | 3 4 1 | 7 | 1.358 | 1.359 | 0 10 1 |
| 14 | 2.123 | 2.123 | 3 0 3 | 5 | 1.328 | 1.328 | 3 5 4 |
| 6 | 2.114 | 2.113 | 2 4 2 | 2 | 1.325 | 1.325 | 5 7 0 |
| 13 | 2.051 | 2.051 | 2 2 3 | 4 | 1.314 | 1.313 | 10 1 0 |
| 19 | 2.043 | 2.043 | 5 1 2 | 2 | 1.308 | 1.308 | 3 8 2 |
| 7 | 2.025 | 2.024 | 6 1 1 | 5 | 1.274 | 1.274 | 5 0 5 |

Cu*K*α (Ni-filtered) $\lambda = 1.5406$ Å; data for intensities > 2%; outlier rejected data (2σ) not listed; calculated powder pattern from single-crystal structure refinement used to aid indexing; no internal standard; $a = 15.978(1)$, $c = 7.172(1)$ Å, $V = 1585.6(4)$ Å$^3$

## TABLE 3. MISCELLANEOUS INFORMATION FOR FLUOR-DRAVITE

| | | | |
|---|---|---|---|
| *a* (Å) | 15.955(3) | crystal size (μm) | 230 sphere |
| *c* | 7.153(2) | radiation/monochromater | Mo$K\alpha$□/Graphit |
| *V* (Å$^3$) | 1576.9(6) | No. unique reflections | 1139 |
| | | No. $I_o$□ > 3σ*I* | 1137 |
| Space Group | *R*3*m* | $R_{\mathbf{az}}$ % | 1.4 → 1.0 |
| Z | 3 | $R_{\mathbf{obs}}$ % | 1.6 |
| $D_{calc}$ (g cm$^{-3}$) | 3.120 | $R_{\mathbf{all}}$ % | 2.6 |
| | | GOF | 2.69 |

## TABLE 4. ATOM POSITIONS AND EQUIVALENT ISOTROPIC-DISPLACEMENT FACTORS IN FLUOR-DRAVITE

| | *x* | *y* | *z* | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| X | 0 | 0 | 0.84080 | 0.0209(6) |
| Y | 0.06312(2) | 0.93688(2) | 0.44473(31) | 0.0088(2) |
| Z | 0.26174(4) | 0.29827(4) | 0.45757(30) | 0.0071(2) |
| T | 0.19009(3) | 0.19191(3) | 0.07041(30) | 0.0067(2) |
| B | 0.88998(10) | 0.11002(10) | 0.61615(46) | 0.0082(7) |
| O(1) | 0 | 0 | 0.29119(48) | 0.0197(8) |
| O(2) | 0.93841(6) | 0.06159(6) | 0.59029(38) | 0.0122(6) |
| O(3) | 0.13491(7) | 0.86509(7) | 0.55913(38) | 0.0114(5) |
| O(4) | 0.90702(7) | 0.09298(7) | 0.00075(37) | 0.0109(5) |
| O(5) | 0.09271(7) | 0.90729(7) | -0.02049(37) | 0.0108(5) |
| O(6) | 0.18803(9) | 0.19746(8) | 0.29369(35) | 0.0094(4) |
| O(7) | 0.28527(8) | 0.28493(9) | -0.01074(33) | 0.0092(4) |
| O(8) | 0.27133(9) | 0.21031(9) | 0.62784(34) | 0.0100(4) |

## TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) FOR FLUOR-DRAVITE

| | | | |
|---|---|---|---|
| *X*–O(2) x3 | 2.471(2) | *Y*–O(1) | 2.061(2) |
| *X*–O(4) x3 | 2.813(1) | *Y*–O(2) x2 | 2.014(2) |
| *X*–O(5) x3 | 2.747(1) | *Y*–O(3) | 2.146(1) |
| <*X*–O> | 2.677 | *Y*–O(6) x2 | 2.041(2) |
| | | <*Y*–O> | 2.053 |
| *Z*–O(3) | 1.977(2) | | |
| *Z*–O(6) | 1.858(2) | *T*–O(4) | 1.625(1) |
| *Z*–O(7) | 1.958(2) | *T*–O(5) | 1.639(2) |
| *Z*–O(7) | 1.886(3) | *T*–O(6) | 1.601(3) |
| *Z*–O(8) | 1.921(3) | *T*–O(7) | 1.610(2) |
| *Z*–O(8) | 1.878(2) | <*T*–O> | 1.619 |
| <*Z*–O> | 1.913 | | |
| *B*–O(2) | 1.351(2) | | |
| *B*–O(8) x2 | 1.388(2) | | |
| <*B*–O> | 1.376 | | |

TABLE 6. REFINED SITE-SCATTERING VALUES (SREF; *epfu*), ASSIGNED SITE-POPULATIONS (*apfu*) AND EQUIVALENT SITE-SCATTERING VALUES (EMPA; *epfu*) FOR FLUOR-DRAVITE

|  | SREF | Site population | EMPA |
|---|---|---|---|
| *X* | 10.7(1) | 0.88 Na + 0.04 Ca | 10.5 |
| *Y* | 49.3(3) | 1.30 Mg + 0.87 Fe + 0.58 Al + 0.09 Mn + 0.03 Ti + 0.13 Li | 49.1 |
| *Z* | 78 | 5.43 Al + 0.57 Mg | 77.4 |
| *W** | 9.3(3) | 0.61 F + 0.39 OH | 8.8 |

*The sum F + (OH) is normalized to 1.0 *apfu*.

TABLE 7. BOND-VALENCE (*vu*)* TABLE FOR ORDERED FLUOR-DRAVITE

| | *X* | *Y* | *Z* | *T* | *B* | Σ |
|---|---|---|---|---|---|---|
| O(1) | | 0.304 $^{x3}\rightarrow$ | | | | 0.912 |
| O(2) | 0.158 $^{x2}\downarrow$ | 0.431 $^{x2}\downarrow$ | | | 1.056 | 2.076 |
| O(3) | | 0.302 | 0.414 | | | 1.130 |
| O(4) | 0.061 $^{x2}\rightarrow$ | | | 0.944 $^{x2}\rightarrow$ | | 2.010 |
| O(5) | 0.074 | | | 0.957 $^{x2}\rightarrow$ | | 1.988 |
| O(6) | | 0.401 $^{x2}\downarrow$ | 0.572 | 1.061 | | 2.034 |
| O(7) | | | 0.436<br>0.530 | 1.035 | | 2.001 |
| O(8) | | | 0.482<br>0.541 | | 0.955 $^{x2}\downarrow$ | 1.978 |
| Σ | 0.879 | 2.270 | 2.975 | 3.997 | 2.966 | |

*Calculated from the curves of Brown & Altermatt (1985)