

Fluor-elbaite, lepidolite and Ta–Nb oxides from a pegmatite of the 3000 Ma Sinceni Pluton, Swaziland: evidence for lithium–cesium–tantalum (LCT) pegmatites in the Mesoarchean

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Abstract: Mineral evolution is concerned with the timing of mineral occurrences, such as the earliest reported occurrences in the geologic record. Minerals containing essential Li have not been reported from rocks older than *ca.* 3000 Ma, thus the lithian tourmaline (fluor-elbaite) and mica (lepidolite) assemblage from a pegmatite near Zishineni associated with the *ca.* 3000 Ma Sinceni Pluton presents unusual interest. Fluor-elbaite (0.75–0.98 F per formula unit) forms green crystals up to 50 mm long. Spindle stage measurements give $\omega = 1.652(1)$, $\varepsilon = 1.627(1)$ (589.3 nm). Optical absorption spectroscopy shows Fe and Mn are divalent; infra-red spectroscopy demonstrates the presence of Li and indicates the presence of (OH) at both the (OH) sites. Electron microprobe analysis of 330 points on several prisms, the largest of which is zoned in Fe and Ca, gives the following average and standard deviations in wt%: SiO₂ 37.29 (0.26), TiO₂ 0.05 (0.05), Al₂O₃ 38.14 (0.35), Cr₂O₃ 0 (0.02), MgO 0.02 (0.01), MnO 3.57 (0.25), FeO 2.48 (0.60), Na₂O 2.48 (0.09), K₂O 0.03 (0.12), CaO 0.77 (0.21), F 1.80 (0.11), Cl 0 (0.01) wt%. Nuclear reaction analyses gave Li₂O 0.91 (0.04) and B₂O₃ 10.55 (0.45). The empirical formula of fluor-elbaite was determined by integrating crystal-chemical data from electron microprobe analysis, nuclear reaction analysis, crystal structure refinement using X-ray diffraction, infra-red and optical absorption spectroscopy: $X(\square_{0.09}\text{Na}_{0.77}\text{K}_{0.01}\text{Ca}_{0.13})\Sigma_{1.00} Y(\square_{0.35}\text{Li}_{0.59}\text{Mn}_{0.49}^{2+}\text{Fe}_{0.33}^{2+}\text{Al}_{1.23}\text{Ti}_{0.01})\Sigma_{3.00}\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3^{03}(\text{OH})_3^{01}[\text{F}_{0.92}(\text{OH})_{0.08}]\Sigma_{1.00}$. The crystal structure of fluor-elbaite was refined to statistical indices *R*₁ for 1454 reflections $\sim 2\%$ using MoK α X-ray intensity data. Structural data confirm the presence of significant vacancies at the *Y* site. Micas include lepidolite in flakes several millimeters across that are veined and overgrown by fine-grained muscovite. Silica and (FeO + MnO) increase, and Al decreases with F, all giving tight linear fits for both micas taken together, suggesting both micas can be regarded as interstratified muscovite and lithium mica consisting of 35.2 wt% masutomilite containing nearly equal amounts of Mn and Fe, 52.8 wt% polyolithionite and 11.9 wt% trilithionite. Muscovite and lepidolite contain < 0.2 wt% and 0.7–2.25 wt% Cs₂O and 1.0–1.1 wt% and 1.4–1.5 wt% Rb₂O, respectively. Other minerals include spessartine (*e.g.*, $\text{Sps}_{93}\text{Alm}_4\text{Grs}_3$) in scattered grains up to 0.5 mm across and monazite. Oxides occur sparsely in muscovite, rarely in lepidolite, as grains up to 11 μm long, including fluorcalciomicrolite, columbite-(Mn) with Nb $>$ Ta, hübnerite(?) and a possible Pb-bearing microcline (Ta $>$ Nb). The oxides, together with the muscovite, are interpreted to be related to later hydrothermal reworking of the primary lepidolite–fluor-elbaite assemblage. Given the 2990 ± 43 Ma Rb–Sr isochron and 3074 ± 4 Ma evaporation Pb–Pb ages reported for the Sinceni Pluton and Rb/Sr mineral ages ranging from 2906 ± 31 Ma to 3072 ± 33 Ma reported for the pegmatites, the fluor-elbaite–cesian lepidolite–fluorcalciomicrocline-bearing pegmatite is the first reported occurrence of a lithian tourmaline and lepidolite in the geologic record, as well as one of the two earliest known examples of the lithium–cesium–tantalum (LCT) family of pegmatites. The Sinceni magma is most plausibly derived from a metasedimentary source by intrusion of hot mantle melts into the crust from below, thereby indicating that a “mature” continental crust existed in the Kaapvaal craton at *ca.* 3000 Ma.

Key-words: mineral evolution; lithium; cesium; tantalum; tourmaline; mica; pegmatite; crystal structure; optical spectroscopy; infrared spectroscopy.

1. Introduction

In their reviews of the temporal distribution of rare-metal pegmatites, Tkachev (2011) and McCauley & Bradley (2014) reported that three of the four oldest pegmatites to

contain beryl and minerals of Li, Sn and Ta are found in the Barberton greenstone belt and neighboring Swaziland, and are dated at 2990–3113 Ma; the fourth being in the Ivissartok area near Nuuk in southwestern Greenland. Among these are granitic pegmatites associated with the

S-type Sinceni Pluton (Trumbull, 1993) which is the subject of this paper. Many pegmatites in this region contain minor beryl and cassiterite mineralization, but are otherwise not chemically specialized. An exception is the Sinceni field with a Li-rich pegmatite near Zishineni (Trumbull, 1993). No occurrence older than 3000 Ma of a mineral containing Li as an essential constituent has been reported in the geological record, *e.g.*, tourmaline formed at 3230 Ma in the Barberton greenstone belt and at 3550 Ma in the Isua supracrustal belt (Greenland) comprise six species lacking essential Li (Grew *et al.*, 2016). Like Be (Grew & Hazen, 2014) and Hg (Hazen *et al.*, 2012), Li minerals have not been found in rocks preserved from the first one third of Earth's history. The appearance of minerals containing these elements suggests that 3000 Ma could be dating an important change in the evolution of Earth's minerals.

Study of a specimen from the Zishineni pegmatite not only confirmed the presence of a Li tourmaline (fluor-elbaite) and lepidolite, but also revealed a significant Cs content in lepidolite and traces of Ta–Nb–W oxides in the pegmatite. The present paper reports detailed mineralogical data for fluor-elbaite, and lepidolite, together with preliminary data on associated Ta–Nb oxides as evidence that the Zishineni pegmatite is one of the earliest known examples of the lithium–cesium–tantalum (LCT) family (*e.g.*, Černý & Ercit, 2005).

2. Occurrence and mineralogy

The pegmatite sample (Bavarian State Museum No. 35177, originally 4576, Technische Universität München) was collected in the Sinceni pegmatite field on Zishineni Ridge north of the Mhlathuzane River near Kubuta, Swaziland; coordinates 26°50'1" S, 31°27'55" E. The pegmatites and the parental Sinceni granite have been described by Trumbull (1993, 1995a and b). The granite and its pegmatites were dated using the Rb–Sr method by Trumbull (1993) and found to be coeval within the uncertainty. The whole-rock Rb–Sr isochron age of the granite is 2990 ± 43 Ma (8 samples, MSWD = 0.8). There is a corroborative age of zircon from the granite (^{206}Pb – ^{207}Pb “evaporation age”, 3074 ± 4 Ma) by Maphalala & Kröner (1993). The Rb/Sr mineral ages of muscovite and K-feldspar from four pegmatite dikes range from 2906 ± 31 Ma to 3072 ± 33 Ma for five of seven separates. K-feldspar in two dikes yielded 2651 ± 30 Ma and 2784 ± 30 Ma, but two other mineral separates from the latter dike gave 3072 ± 33 Ma and 3060 ± 50 Ma, consequently the younger ages were attributed to some loss of radiogenic Sr (Trumbull, 1993). These are not precise ages but their agreement with one another and with the Sinceni granite lends confidence to an age assignment for the pegmatite field of 2900–3100 Ma.

The common pegmatites at the Zishineni locality and elsewhere in the Sinceni field are quartz–K-feldspar–albite–muscovite–schorl assemblages with accessory cassiterite, which has been mined at a small scale in alluvial workings. Trumbull (1993) noted that the “elbaite” (fluor-elbaite) and Li-rich mica assemblage

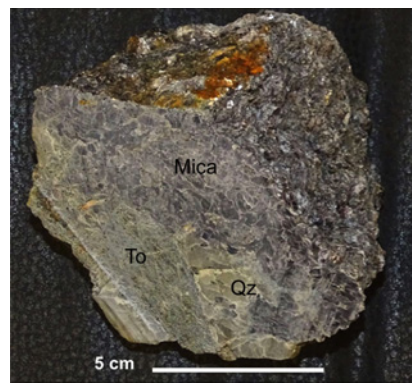


Fig. 1. Specimen (Bavarian State Museum No. 35177, originally 4576, Technische Universität München) of the pegmatite from the Sinceni pegmatite field on Zishineni Ridge. To – fluor-elbaite, Qtz – quartz, mica – aggregate of lepidolite with subordinate muscovite.

partly replaced quartz–feldspar–schorl pegmatite at this locality and produced extensive quartz–Li mica metasomatism of the metatonalite host rock. This may be analogous to the late-stage, discordant albite–lepidolite bodies in complex zoned pegmatites; these bodies form by residual melt and/or fluid from internal units that is injected into and reacts with outer zones and wallrocks (London, 2014). Based on a study of fluid inclusions, Trumbull (1995a) estimated crystallization of the late-stage fluor-elbaite at 450–550 °C and 4–5 kbar.

The specimen studied here (approximately 5 cm × 6 cm × 7 cm in size, Fig. 1) consists mainly of a dense intergrowth of lepidolite (euhedral grains 1–5 mm), with subordinate quartz (anhedral grains, 5–20 mm) and green fluor-elbaite (euhedral grains, up to 50 mm length). A thin section dominated by fluor-elbaite and quartz with much subordinate lepidolite and muscovite was the main object for this study. About half of the section is taken up by part of one crystal of fluor-elbaite (in hand specimen: 50 mm in length and 20 mm width), which has some crack-fillings of white mica and/or spessartine, the latter in grains up to 0.5 mm across. A few spessartine grains are also found with lepidolite (Fig. 2b). Other fluor-elbaite crystals 1–2 mm in length are included in quartz. Monazite is rare. Micas include lepidolite in flakes several millimeters across that are veined and overgrown by fine-grained muscovite. Tantalum–niobium oxides occur sparsely in muscovite, rarely in lepidolite, as grains up to 11 µm long. Microstructures suggest a two-staged evolution of the pegmatite assemblages: the original assemblage fluor-elbaite–lepidolite–quartz was hydrothermally worked, resulting in the precipitation of muscovite, Ta–Nb oxides and spessartine.

3. Methods

3.1. Electron microprobe analysis

Compositions of fluor-elbaite, spessartine, lepidolite and oxides were determined using the Cameca SX100 electron microprobe and wavelength dispersive spectroscopy at the

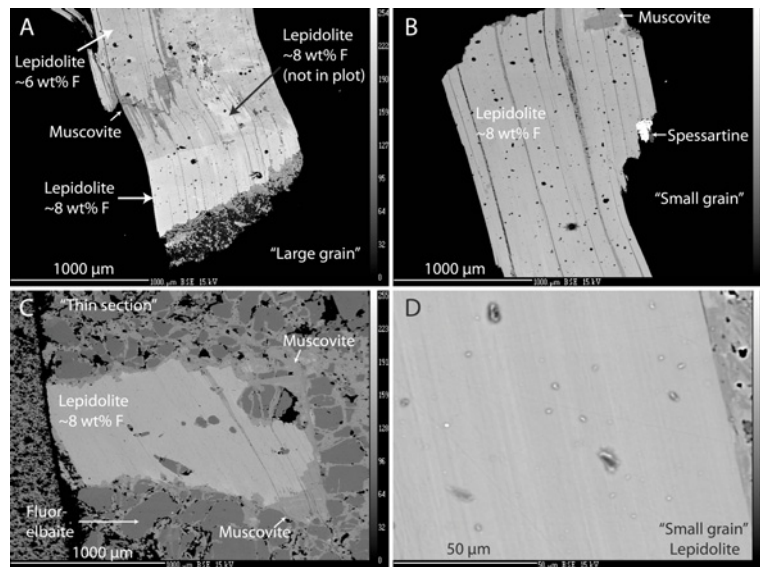


Fig. 2. Back-scattered electron images of lepidolite and muscovite. (a, b) Mica flakes showing two compositionally distinct varieties of lepidolite as well as later muscovite from the lepidolite aggregate (Fig. 1); (c) micas associated with fluor-elbaite in the thin section; (d) lepidolite at high magnification to illustrate fine layering.

University of Maine. The operating conditions were a 15 kV acceleration voltage, 10 nA beam current and a 5 µm beam diameter for the silicates. Counting times were 20 s on peak and 10 s on background on either side of the peak, except for F, where counting times were 40 s and 20 s, respectively. Analyses of fluor-elbaite were carried out in two sessions, one on February 3, 2016 with the standards polyolithionite (FKα), tugtupite (NaKα, ClKα), diopside (MgKα, CaKα), anorthite (AlKα, SiKα), sanidine (KKα), rutile (TiKα), Cr₂O₃ (CrKα), rhodonite (MnKα), and almandine (FeKα). The second session on February 10, 2016, included the additional standards barite (BaLα) and pollucite (RbLα, CsLα). The analyses gave 0.4 wt% Rb₂O, which was discarded as meaningless because of difficulties in calibrating Rb (see below). The set up for muscovite and lepidolite was the same as for fluor-elbaite, except that sanidine was substituted for anorthite to calibrate Si in lepidolite, because of its relatively high SiO₂ content. A different set of elements was measured in spessartine: tugtupite (NaKα), pyrope (MgKα), almandine (AlKα, SiKα, FeKα), diopside (CaKα), rutile (TiKα), Cr₂O₃ (CrKα), rhodonite (MnKα), and yttrium-aluminum garnet (YLα). In contrast to the silicates, the oxides were analyzed with a focused beam because the grains were so small. The following element set was measured: polyolithionite (FKα), tugtupite (NaKα), spinel (MgKα, AlKα), sanidine (KKα), scheelite (CaKα, WaLα), rutile (TiKα), rhodonite (MnKα), magnetite (FeKα), LiNbO₃ (NbLα), cassiterite (SnLα), LiTaO₃ (TaLα), and crocoite (PbMα). Data were processed using the X-Phi correction of Merlet (1994).

Analysis of Rb in the micas required special treatment because the RbLα peak is located on the low energy tail of the SiKα peak. Strong spectral interference from Si and the lack of a primary standard with high concentrations of Rb necessitated analysis using spectral scans. A large area

TAP crystal spectrometer was scanned through the interval containing RbLα and SiKα. The spectra were deconvolved assuming a Voigt peak shape into constituent peaks. Pollucite containing 0.70 wt% Rb was similarly scanned and processed. Calculated intensity ratios (*k*-ratios) were matrix corrected and converted into oxide weight%.

Micas were not analyzed for Li, instead it was estimated from the contents of other constituents. Several empirical relationships have been applied to estimating Li₂O content based on constituents, such as F, MgO, FeO and SiO₂, measurable with the electron microprobe (e.g., Tindle & Webb, 1990; Tischendorf *et al.*, 1997). However, analyses of our lithian micas gave such highly regular relationships between F content on the one hand, and SiO₂, Al₂O₃ and (MnO + FeO + MgO) contents on the other (Fig. 3) that we estimated Li₂O contents from the proportions of masutomilite (KLiAlMn²⁺(Si₃Al)O₁₀F₂), as formulated by Brigatti *et al.*, 2007), polyolithionite (KLi₂AlSi₄O₁₀F₂), and trilithionite (KLi_{1.5}Al_{1.5}(Si₃Al)O₁₀F₂) in terms of their ideal formulations. The least squares fit of the data in Fig. 3c gives 5.75 wt% (MnO + FeO + MgO) for F = 8.68 wt%, the ideal F content of masutomilite containing roughly equal amounts of MnO and FeO (MgO contents are negligible). This corresponds to 35.2 wt% masutomilite in the mix of Li mica components assuming all the MnO, FeO and MgO is in the masutomilite component, ideally KLiAl(Mn²⁺, Fe²⁺, Mg)(Si₃Al)O₁₀F₂. To calculate the proportions of trilithionite and polyolithionite, ideally KLi_{1.5}Al_{1.5}(Si₃Al)O₁₀F₂ and KLi₂AlSi₄O₁₀F₂, respectively, we took the average F content for these two components, 9.63 wt%, for which the least square fits in Fig. 3a and b gave 52.17 wt% SiO₂ and 18.62 wt% Al₂O₃, respectively. This SiO₂ content is calculated to result from a mix of 35.2 wt% masutomilite, 54.4 wt% polyolithionite and 10.3 wt% trilithionite, and the Al₂O₃ content, from a mix of 35.2 wt% masutomilite,

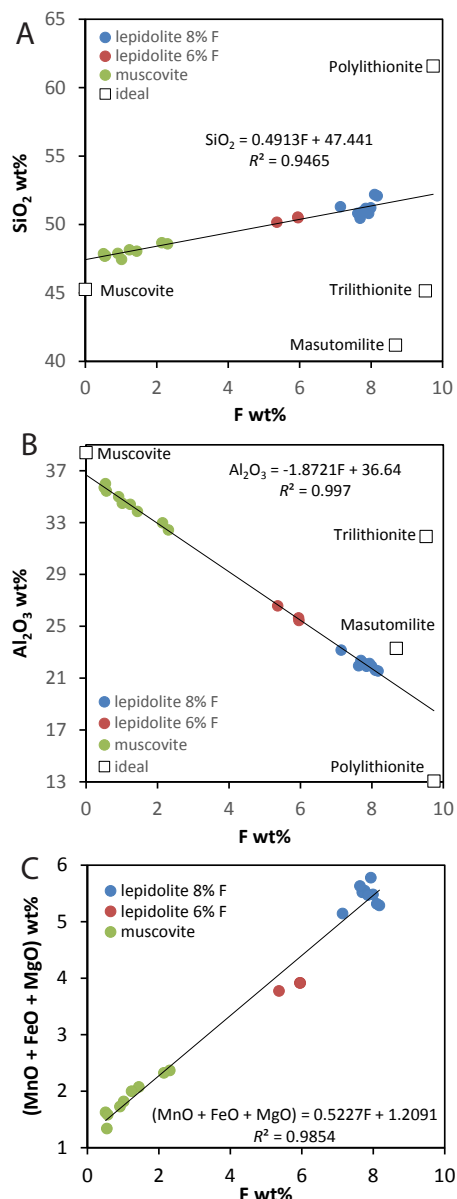


Fig. 3. Variation of SiO_2 , Al_2O_3 and $(\text{MnO} + \text{FeO} + \text{MgO})$ contents as a function of F used for calculating Li_2O contents.

51.2 wt% polyolithionite and 13.5 wt% trilithionite. We chose an average of the two mixes for the calibration, *i.e.*, 35.2 wt% masutomilite, 52.8 wt% polyolithionite and 11.9 wt% trilithionite. These proportions of the three components give 9.34 wt% F and 5.92 wt% Li_2O . Thus the measured F content in all our micas could be used to calculate Li_2O contents: $\text{Li}_2\text{O} = \text{F}/9.34 \times 5.92$ in wt%.

3.2. Nuclear microprobe analysis

The nuclear microprobe analysis for quantification of lithium (^7Li) and boron (^{11}B) was conducted at The Lund Ion Beam Analysis Facility, Lund, Sweden. Before the analysis a crystal of fluor-elbaite ($400 \mu\text{m} \times 400 \mu\text{m}$) was embedded in epoxy and polished down to a flat surface.

For the measurement an 850 keV proton beam, focused to a beam spot size of about $50 \mu\text{m} \times 50 \mu\text{m}$, was directed perpendicular to the sample surface. The surface of the crystal was then scanned by magnetic deflection of the beam. If the incident protons encounter a Li or B atom in the sample it induces a nuclear reaction. The reactions are very specific for the isotopes of the two chemical elements. By measuring the reaction products, a nearly background-free signal of the Li and B content in the sample is achieved. This signal is not influenced by orientation or structural defects of the crystal. The system has a minimum detection limit of 1 ppm weight for both Li and B (Nilsson *et al.*, 2017; De La Rosa *et al.*, 2017).

The measured quantity is in units of Li or B atoms per cm^2 and later converted into ppm weight by the use of three calibration crystals for each element: Li: NIST SRM 610 (National Institute of Standards & Technology, 2012a); NIST SRM 612 (National Institute of Standards & Technology, 2012b), and Li phosphate (Li_3PO_4); B: NIST SRM 610, NIST SRM 612, and tourmaline (Skogby *et al.*, 2003). The elemental content of the standards ranges from 40 ppm weight to 17.98 wt% Li and 32 ppm weight to 3.27 wt% B. The calibration procedure is further described in Nilsson *et al.* (2017) and De La Rosa *et al.* (2017).

Due to the small size of the crystal, not all of the embedding epoxy could be removed from the crystal surface, resulting in a very small measurable area and consequently no boron and lithium distribution maps could be acquired.

3.3. Fourier transform infrared spectroscopy (FTIR) for tourmaline

Polarized FTIR-spectra were measured at the Swedish Museum of Natural History with a $40 \mu\text{m} \times 80 \mu\text{m}$ aperture in the range $600\text{--}5000 \text{ cm}^{-1}$ using a Bruker Hyperion 2 FTIR microscope spectrometer equipped with a halogen lamp source, a KBr beam-splitter, a holographic ZnSe polarizer and a midband MCT detector on a thin ($\sim 15 \mu\text{m}$) tourmaline fragment extracted from the polished thin section and further thinned and polished to remove the embedding medium (epoxy).

3.4. Visible light spectroscopy for tourmaline

Polarized optical absorption spectra of the absorber used in the FTIR experiments were recorded at the Swedish Museum of Natural History in the range $8000\text{--}34\,000 \text{ cm}^{-1}$ using an AVASPEC-ULS2048 $\times$ 16 spectrometer and a thermo-electric cooled AVASPEC NIR256-1.7 TEC spectrometer attached via $400 \mu\text{m}$ UV and IR fiber cables to a Zeiss Axiotron UV-microscope. A 75 W Xenon arc lamp and 100 W halogen lamp was used as a light sources and Zeiss Ultrafluor $10\times$ lenses served as objective and condenser. The size of the circular measurement aperture was $64 \mu\text{m}$ in diameter. A UV-quality Glan-Thompson prism with a working range from 250 nm to 2700 nm ($40\,000 \text{ cm}^{-1}$ to 3704 cm^{-1}) was used as polarizer.

3.5. Single-crystal structure refinement (SREF) of tourmaline

A crystal fragment extracted from the polished thin section of the tourmaline-bearing specimen was selected for single-crystal X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer (Sapienza University of Rome, Earth Sciences Department), equipped with a CCD area detector ($6.2 \times 6.2 \text{ cm}^2$ active detection area, 512×512 pixels) and a graphite-crystal monochromator, using MoK α radiation from a fine-focus sealed X-ray tube (Table 1). The sample-to-detector distance was 4 cm. A total of 2631 exposures (step = 0.3° , time/step = 20 s) covering a full reciprocal sphere with a redundancy of about 7 were collected and a completeness of 97% was achieved. Final unit-cell parameters were refined by using the Bruker AXS SAINT program on reflections with $I > 10 \sigma(I)$ in the range $6^\circ < 2\theta < 70^\circ$. The intensity data were processed and corrected for Lorentz, polarization and background effects with the APEX2 software program of Bruker AXS. The data were corrected for absorption using a multi-scan method (SADABS). The absorption correction led to a significant improvement in R_{int} . No violations of $R3m$ symmetry were noted.

Structure refinement was done with the SHELXL-2013 program (Sheldrick, 2013). Starting coordinates were taken from Bosi *et al.* (2016). Variable parameters were: scale factor, atomic coordinates, site scattering values expressed as mean atomic number (m.a.n.) for the X and Y sites, and atomic displacement factors. Neutral scattering curves were used for all atoms. The X site was modeled considering the presence of Na, Ca and vacancy ($\square$). The Z , T , B and $O1$ sites were modeled, respectively, with Al, Si, B and F scattering factors and with a fixed occupancy of 1, because refinement with unconstrained occupancies showed no significant deviations from this value. Chemical analyses showed the Y site occupancy to approximate $Y = (\square_{0.35}\text{Li}_{0.59}\text{Mn}_{0.49}\text{Fe}_{0.34}\text{Al}_{1.23})$, see below. Accordingly, the Y site was refined by setting the Li and Mn occupancy to 0.59 apfu and 0.49 apfu (respectively) and allowing the remaining cations of the site to refine as $\text{Al} = (1.57 - \text{Fe})$ apfu. The position of the H atom bonded to the oxygen at the $O3$ site in the structure was taken from the difference-Fourier map and incorporated into the refinement model. Following the findings of Burns *et al.* (1994) who reported high U_{eq} values for the $O1$ and $O2$ sites that indicate position disorder, the crystal was refined twice, (1) with both sites constrained to their positions of maximum site-symmetry, $(0\ 0\ z)$ for $O1$ and $(x, 1-x, z)$ for $O2$, and (2) with both sites allowed to disorder with coordinates $(x, x/2, z)$ and (x, y, z) (referred as split-site SREF in this work). There were no correlations greater than 0.7 between the parameters at the end of the refinement. Table 1 lists crystal data, data collection information and refinement details; Table 2 gives the fractional atomic coordinates, equivalent displacement parameters and site occupancies; Table 3 shows selected bond lengths. Anisotropic displacement parameters (Table S1, Appendix S1) and CIF file (Table S2,

Table 1. X-ray diffraction data for the fluor-elbaite studied (sample-b).

Crystal size (mm)	$0.38 \times 0.35 \times 0.03$	
a (Å)	15.9034(4)	
c (Å)	7.1238(2)	
V (Å ³)	1560.35(9)	
Range for data collection, 2θ ($^\circ$)	5–70	
Reciprocal space range hkl	$-25 \leq h \leq 25$; $-25 \leq k \leq 25$; $-11 \leq l \leq 10$	
Total number of frames	2631	
Set of measured reflections	5590	
Unique reflections, R_{int} (%)	1454, 2.60	
Data completeness to theta max (%)	97	
Absorption correction method	Multiscan (SADABS)	
Refinement method	Least-squares on F^2	
Structural refinement program	SHELXL-2013	
	Standard SREF ^a	Split-site SREF ^b
Flack parameter	0.04(5)	0.04(4)
wR2 (%)	5.19	4.80
R1 (%) all data	2.23	2.01
R1 (%) for $I > 2\sigma(I)$	2.14	1.92
Goof	1.107	1.062
Largest diff. peak and hole ($\text{e} \text{ \AA}^{-3}$)	1.26 and -0.79	0.59 and -0.43

Notes: R_{int} = merging residual value; $R1$ = discrepancy index, calculated from F -data; $wR2$ = weighted discrepancy index, calculated from F^2 -data; radiation, MoK α = $0.71073 \text{ \AA}$. Data collection temperature = $293(2) \text{ K}$. Space group $R3m$; $Z = 3$.

^a Standard SREF denotes structural refinement done with $O1$ at $(0, 0, z)$ and $O2$ at $(x, 2x, z)$.

^b Split-site SREF denotes structural refinement done with $O1$ at $(x, 2x, z)$ and $O2$ at (x, y, z) to allow for positional disorder, as indicated by the high U_{eq} values (Burns *et al.*, 1994).

Appendix S1) are provided as supplementary material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org>.

4. Results

4.1. Tourmaline

4.1.1. Chemical composition and structure refinement

Chemical data (Table 4) showed the tourmaline to be Na- and F-dominant with sufficient Li to give fluor-elbaite as the dominant component, with subordinate fluor-tsilasite, fluor-schorl and a component with a vacancy at the Y site, ideally $^{\text{X}}\text{Na}^{\text{Y}}(\square\text{Al}_2)_{\Sigma 3.00}\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3\text{O}^3(\text{OH})_3\text{F}$, respectively, 39%, 16%, 11% and 34% for the average of 330 analyses on February 3. Some heterogeneity in F (1.48–1.92 wt%), Na_2O (2.35–2.75 wt%), CaO (0.22–1.12 wt%) and FeO (1.08–3.31 wt%) is revealed in both the quantitative analyses (e.g., Table 4) and in chemical maps of the largest crystal, which has a Ca-poorer rim about 1 mm thick and less regularly distributed Fe-poorer patches. Zoning in Mn is barely perceptible (3.09–3.90 wt% MnO). The February 10 electron microprobe session gave

Table 2. Fractional atomic coordinates (x, y, z), equivalent isotropic displacement parameters (U_{eq} in $\text{\AA}^2$) and site occupancies for the fluor-elbaite studied (sample-b).

Site	x	y	z	U_{eq}	Site occupancy
<i>Standard SREF</i>					
X	0	0	0.2339(4)	0.0219(9)	$\text{Na}_{0.769(17)}\text{Ca}_{0.143(17)}\square_{0.088}$
Y	0.12412(7)	0.06206(3)	0.62734(16)	0.0096(3)	$\text{Al}_{0.403(5)}\text{Fe}_{0.123(5)}\text{Mn}_{0.162}\text{Li}_{0.196}\square_{0.115}$
Z	0.29763(4)	0.26081(5)	0.61171(13)	0.00679(12)	$\text{Al}_{1.00}$
B	0.10951(11)	0.2190(2)	0.4549(5)	0.0065(5)	$\text{B}_{1.00}$
T	0.19203(4)	0.19008(4)	0	0.00570(10)	$\text{Si}_{1.00}$
O1 ($\equiv W$)	0	0	0.7840(7)	0.0622(18)	$\text{F}_{1.00}$
O2	0.06080(8)	0.12159(17)	0.4820(4)	0.0192(5)	$\text{O}_{1.00}$
O3 ($\equiv V$)	0.26905(18)	0.13452(9)	0.5097(3)	0.0106(4)	$\text{O}_{1.00}$
O4	0.09296(8)	0.18592(17)	0.0717(3)	0.0096(4)	$\text{O}_{1.00}$
O5	0.18600(16)	0.09300(8)	0.0936(3)	0.0099(4)	$\text{O}_{1.00}$
O6	0.19715(10)	0.18714(10)	0.7755(2)	0.0086(3)	$\text{O}_{1.00}$
O7	0.28569(10)	0.28583(10)	0.0806(2)	0.0077(3)	$\text{O}_{1.00}$
O8	0.20991(11)	0.27054(11)	0.4415(2)	0.0088(3)	$\text{O}_{1.00}$
H3	0.263(3)	0.1316(16)	0.397(6)	0.013 ^a	$\text{H}_{1.00}$
<i>Split-site SREF</i>					
X	0	0	0.2341(3)	0.0207(8)	$\text{Na}_{0.776(13)}\text{Ca}_{0.137(13)}\square_{0.087}$
Y	0.12415(6)	0.06207(3)	0.62733(14)	0.0099(2)	$\text{Al}_{0.397(4)}\text{Fe}_{0.129(4)}\text{Mn}_{0.162}\text{Li}_{0.196}\square_{0.115}$
Z	0.29762(4)	0.26080(4)	0.61174(11)	0.00672(11)	$\text{Al}_{1.00}$
B	0.10948(10)	0.2190(2)	0.4551(4)	0.0069(4)	$\text{B}_{1.00}$
T	0.19202(3)	0.19007(3)	0	0.00558(9)	$\text{Si}_{1.00}$
O1 ($\equiv W$)	0.0240(3)	0.01198(14)	0.7844(6)	0.0145(11) ^a	$\text{F}_{0.33}$
O2	0.0701(2)	0.12177(15)	0.4823(3)	0.0106(5) ^a	$\text{O}_{0.50}$
O3 ($\equiv V$)	0.26917(15)	0.13458(8)	0.5097(3)	0.0106(3)	$\text{O}_{1.00}$
O4	0.09296(7)	0.18593(14)	0.0717(3)	0.0095(3)	$\text{O}_{1.00}$
O5	0.18590(14)	0.09295(7)	0.0934(3)	0.0099(3)	$\text{O}_{1.00}$
O6	0.19708(9)	0.18705(9)	0.7755(2)	0.0087(2)	$\text{O}_{1.00}$
O7	0.28574(9)	0.28589(8)	0.08059(19)	0.0077(2)	$\text{O}_{1.00}$
O8	0.20986(9)	0.27056(9)	0.4416(2)	0.0087(2)	$\text{O}_{1.00}$
H3	0.264(3)	0.1319(13)	0.398(5)	0.013 ^a	$\text{H}_{1.00}$

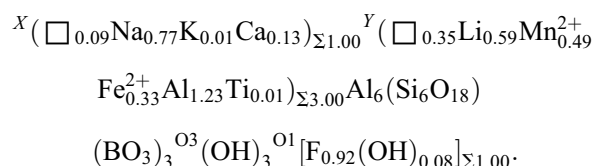
Notes: Standard and split-site SREF denote, respectively, structural refinements carried out with the O1 site at (0, 0, z) and the O2 site at ($x, 2x, z$), and with O1 at ($x, x/2, z$) and O2 at (x, y, z) to allow for positional disorder, as indicated by the high U_{eq} values (Burns *et al.*, 1994). H-atom was constrained to have an isotropic displacement parameter 1.2 times the U_{eq} value of the O3 oxygen.

^a Isotropic displacement parameter.

somewhat higher Al_2O_3 and lower SiO_2 contents than the February 3 session. Barium and Cs were also measured during the February 10 session, which yielded 0–0.06 wt% BaO and 0.02–0.05 wt% Cs_2O , values not included in Table 4.

Atomic fractions of fluor-elbaite were determined by integrating compositional data from electron microprobe analysis, nuclear reaction analysis, crystal structure refinement using X-ray diffraction, and spectroscopy, specifically, optical absorption spectroscopy shows Fe and Mn are divalent and infrared spectroscopy demonstrates the presence of (OH) at both the O1 and O3 sites. The structure-refinement suggests that B and Si contents are stoichiometric, *i.e.*, B = 3.00 atoms per formula unit (apfu) and Si = 6.00 apfu. The mean atomic number of the B and T sites are 5 and 14 (respectively), the mean bond distance of $\langle B-O \rangle$ and $\langle T-O \rangle$ (1.376 Å and 1.620 Å, respectively) are typical of B and T sites fully populated by B^{3+} and Si^{4+} , respectively (*e.g.*, MacDonald & Hawthorne, 1995; Bosi & Lucchesi, 2007). The amount of (OH) was then calculated by stoichiometry.

With regard to the SREF-fragment sample-b, the average composition of 330 analytical points (Table 4) obtained on February 3 was found to be coherent with SREF results. In particular, there is an excellent match between the number of electrons per formula unit (epfu) derived from chemical and structural analysis (227.6 epfu and 227.1 epfu, respectively). The combination of the crystal-chemical analyses resulted in the empirical structural formula:



The bond-valence analysis carried out by bond-valence parameters from Brown & Altermatt (1985) is consistent with the structural formula. In particular, using the equation for the $^w(\text{OH})$ calculation [$^w(\text{OH}) = 2 - 1.01 \text{BVS}^*(\text{O1}) - 0.21 - \text{F}$ (Bosi, 2013)], the bond-valence

Table 3. Selected bond distances (Å) for the fluor-elbaite studied (sample b).

	Standard SREF	Split-site SREF
X-O2 (×3)	2.435(3)	2.441(3)
X-O5 (×3)	2.750(2)	2.750(2)
X-O4 (×3)	2.809(3)	2.810(2)
⟨X-O⟩	2.665	2.667
Y-O2 (×2)	1.9838(18)	Y-O1 1.776(4)
Y-O6 (×2)	2.0271(17)	Y-O2 (×2) 1.877(3)
Y-O1	2.042(3)	Y-O6 (×2) 2.0261(15)
Y-O3	2.165(3)	Y-O2 (×2) 2.096(3)
⟨Y-O⟩	2.038	Y-O3 2.166(2)
		Y-O1 (×2) 2.202(3)
Z-O6	1.8481(16)	1.8488(14)
Z-O7	1.8809(15)	1.8809(13)
Z-O8	1.8823(16)	1.8830(14)
Z-O8'	1.9123(16)	1.9125(14)
Z-O7	1.9545(15)	1.9538(13)
Z-O3	1.9636(11)	1.9631(10)
⟨Z-O⟩	1.907	1.907
B-O2	1.356(4)	1.360(3)
B-O8 (×2)	1.386(2)	1.3860(19)
⟨B-O⟩	1.376	1.377
T-O6	1.6034(17)	1.6030(15)
T-O7	1.6121(15)	1.6130(13)
T-O4	1.6258(9)	1.6256(8)
T-O5	1.6398(11)	1.6394(9)
⟨T-O⟩	1.620	1.620

Notes: Standard and split-site SREF denote, respectively, structural refinements carried out with the O1 site at (0, 0, z) and the O2 site at (x, 2x, z), and with O1 at (x, x/2, z) and O2 at (x, y, z) to allow for positional disorder, as indicated by the high U_{eq} values (Burns *et al.*, 1994).

sum (BVS) incident at the O1 site [BVS(O1)=0.84 valence units] yields an $^W(\text{OH})$ value of 0.03 apfu, very close to that of the empirical structural formula (0.08 apfu). Despite the zonation in Fe and Ca, sample-b can be considered representative of the analyzed tourmaline. Its empirical structural formula shows $^Y(2\text{Li})$ contents larger than $^Y\text{R}^{2+}$ (divalent cations), which is typical of a ^XNa -, ^ZAl -dominant tourmaline belonging to the alkali group-subgroup 2 (Henry *et al.*, 2011). As $^W\text{F} > ^W\text{OH}$, the studied sample corresponds to an Fe^{2+} -bearing, Mn^{2+} -rich fluor-elbaite, ideal formula $\text{Na}(\text{Li}_{1.5}\text{Al}_{1.5})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{F}$ (Bosi *et al.*, 2013).

The present fluor-elbaite shows structural parameters similar to other elbaite tourmalines reported in the literature. For instance, the unit-cell parameters of fluor-elbaite from the Sinceni Pluton are within the typical range of elbaite tourmalines: $a \sim 15.78\text{--}15.93 \text{ Å}$, $c \sim 7.09\text{--}7.13 \text{ Å}$ (e.g., Burns *et al.*, 1994; Bosi *et al.*, 2005, 2013; Rozhdestvenskaya *et al.*, 2005; Ertl *et al.*, 2006; Lussier *et al.*, 2011). With respect to the type fluor-elbaite described by Bosi *et al.* (2013), the present fluor-elbaite shows a significant number of vacancies at the Y site (~ 0.3 pfu vs. 0 pfu) and a smaller Li content (~ 0.6 apfu vs. 1.0 apfu). Although other octahedral-vacant tourmalines

dominated by the olenitic, elbaite or schorlitic component have already been reported (e.g., Ertl *et al.*, 1997; Hughes *et al.*, 2000, 2004; Schreyer *et al.*, 2002; Ertl *et al.*, 2006; Filip *et al.*, 2012), the sample from the Sinceni Pluton is the first tourmaline dominated by the fluor-elbaite component having cation vacancies at the Y site. The latter could be incorporated in fluor-elbaite by the mechanism $^Y(2\text{□} + \text{Al}) \rightarrow ^Y(3\text{Li})$ that leads to the hypothetical end-member $\text{Na}(\text{□Al}_2)\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{F}$. In accordance with the bond-valence theory (e.g., Bosi, 2010), cation vacancies at the Y site should be coupled with trivalent cations at the Y and Z sites and monovalent anions at the O1 and O3 sites, forming the cluster $^{\text{O1}}(\text{F})\text{--}^Y(\text{□AlAl})\text{--}^{\text{O3}}(\text{OH}\text{OH}\text{OH})\text{--}^Z(\text{AlAlAlAlAlAl})$.

4.1.2. FTIR and local atomic arrangements around the (OH) sites

In addition to strong bands caused by vibrations in SiO_4 and BO_3 groups, the recorded infrared spectra show strongly polarized bands due to O–H vibrations in the range $3300\text{--}3700 \text{ cm}^{-1}$ (Fig. 4). The E||c spectrum is truncated, but it is evident that three strong bands exist at 3592 cm^{-1} , 3558 cm^{-1} and 3494 cm^{-1} . In addition, there are bands at 3338 cm^{-1} and 3406 cm^{-1} , as well as two very weak bands at 3672 cm^{-1} and 3645 cm^{-1} . The strong bands below 3640 cm^{-1} can be associated with $^V(\text{OH})$ at the O3 site, while the extremely weak bands $>3640 \text{ cm}^{-1}$ are related to $^W(\text{OH})$ at the O1 site (e.g., Gonzalez-Carreño *et al.*, 1988; Skogby *et al.*, 2012).

The very low intensity of these bands is consistent with the dominance of F and minor fractions of (OH) at the W position (i.e., the O1 site) in the tourmaline general formula $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$. In addition, the band at 3672 cm^{-1} can be related to the local arrangements involving Li, $^Y(\text{LiR}^{2+}\text{Al})\text{--}^{\text{O1}}(\text{OH})$, which demonstrates the occurrence of Li in the studied tourmaline, whereas that at 3645 cm^{-1} is related to $^Y(\text{R}^{2+}\text{R}^{2+}\text{R}^{2+})\text{--}^{\text{O1}}(\text{OH})$ (Bosi *et al.*, 2015). In accordance with Watenphul *et al.* (2016), the bands at 3592 cm^{-1} , 3558 cm^{-1} and 3494 cm^{-1} are assigned to the arrangements: $[(^Y\text{Li}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Li}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}^{\text{O3}}(\text{OH})_3]$, $[(^Y\text{R}^{2+}\text{Al}^Z\text{Al})\text{--}(^Y\text{R}^{2+}\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}^{\text{O3}}(\text{OH})_3]$ and $[(^Y\text{Li}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}^{\text{O3}}(\text{OH})_3]$, respectively. The band at 3406 cm^{-1} is assigned to $[(^Y\text{□}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}(^Y\text{Al}^Z\text{Al}^Z\text{Al})\text{--}^{\text{O3}}(\text{OH})_3]$. Although bands in the lowest frequency region (about $3300\text{--}3400 \text{ cm}^{-1}$) were assigned to the occurrence of $^T\text{B}^{3+}$ (e.g., Kutzschbach *et al.*, 2016), we related the band at 3338 cm^{-1} to a generic hydrogen bond $\text{O3--H}\cdots\text{O5}$ (e.g., Bosi *et al.*, 2012) as no $^T\text{R}^{3+}$ -cations occurred in the studied sample.

4.1.3. Optical properties and spectroscopy

The fluor-elbaite is uniaxial (–); $\omega = 1.652(1)$ and $\varepsilon = 1.627(1)$ (589.3 nm), close to $\omega = 1.640(5)\text{--}1.648(2)$ and $\varepsilon = 1.625(5)\text{--}1.629(2)$ measured on the two samples serving as holotype specimens of fluor-elbaite (Bosi *et al.*, 2013). Dichroism was not observed.

Table 4. Fluor-elbaite compositions (electron microprobe analysis; Li and B by nuclear microprobe analysis).

Name	Ave ^a	Stdev ^a	In Qtz ^b	In Qtz ^c	Low Ca ^b	High Fe ^b	High Fe ^c	Low Fe ^b	Low Fe ^c	Right rim
Date	3-Feb	3-Feb	3-Feb	10-Feb	3-Feb	3-Feb	10-Feb	3-Feb	10-Feb	10-Feb
<i>n</i>	330	330	83	40	20	20	10	10	10	30
<i>wt%</i>										
SiO ₂	37.29	0.26	37.37	36.95	37.36	37.27	36.71	37.73	37.03	36.60
TiO ₂	0.05	0.05	0.08	0.05	0.01	0.10	0.10	0.00	0.02	0.03
B ₂ O ₃ calc	10.80	—	10.83	10.83	10.78	10.79	10.78	10.84	10.85	10.80
B ₂ O ₃ meas	10.55	0.45 ^d	10.55	10.55	10.55	10.55	10.55	10.55	10.55	10.55
Al ₂ O ₃	38.14	0.35	38.18	38.77	38.09	37.66	38.30	38.61	39.43	38.95
Cr ₂ O ₃	0.00	0.02	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.02	0.01	0.01	0.00	0.01	0.04	0.03	0.01	0.01	0.01
CaO	0.77	0.21	0.78	0.49	0.48	0.85	0.91	0.64	0.64	0.50
MnO	3.57	0.25	3.46	3.37	3.57	3.41	3.36	3.83	3.79	3.31
FeO	2.48	0.60	2.65	2.64	2.42	3.21	3.07	1.12	1.14	2.78
Li ₂ O	0.91	0.04 ^d	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91
Na ₂ O	2.48	0.09	2.50	2.75	2.59	2.45	2.54	2.42	2.55	2.71
K ₂ O	0.03	0.12	0.02	0.03	0.02	0.07	0.01	0.12	0.01	0.01
F	1.80	0.11	1.77	1.73	1.75	1.86	1.72	1.76	1.63	1.66
Cl	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ Ocalc	2.87	—	2.90	2.92	2.89	2.84	2.91	2.91	2.97	2.94
O=F, Cl	−0.76		−0.75	−0.73	−0.74	−0.78	−0.72	−0.74	−0.69	−0.70
Total ^e	100.46		100.71	100.74	100.14	100.68	100.63	100.16	100.29	100.51
<i>Formulae per 31 anions</i>										
Si	5.999		5.999	5.929	6.022	6.004	5.917	6.048	5.931	5.889
Bcalc	3.000		3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Ti	0.007		0.009	0.006	0.001	0.012	0.012	0.000	0.003	0.004
Al	7.232		7.224	7.334	7.237	7.151	7.275	7.293	7.444	7.388
Cr	0.000		0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000
Li	0.589		0.587	0.587	0.590	0.590	0.590	0.587	0.586	0.589
Mg	0.004		0.002	0.001	0.002	0.009	0.007	0.003	0.001	0.003
Mn	0.487		0.471	0.458	0.487	0.465	0.458	0.519	0.514	0.451
Fe	0.334		0.356	0.354	0.327	0.433	0.414	0.151	0.152	0.374
□ at Y	0.348		0.351	0.255	0.357	0.340	0.243	0.448	0.300	0.192
Sum Y + Z	9.000		9.000	9.000	9.000	9.000	9.000	9.000	9.000	9.000
Na	0.773		0.780	0.855	0.811	0.766	0.793	0.752	0.793	0.846
K	0.007		0.004	0.005	0.004	0.015	0.003	0.024	0.002	0.003
Ca	0.132		0.134	0.084	0.082	0.147	0.157	0.111	0.109	0.086
Sum X	0.913		0.918	0.944	0.897	0.929	0.953	0.887	0.904	0.935
Sum cations	18.563		18.565	18.619	18.562	18.593	18.626	18.487	18.535	18.632
F	0.915		0.899	0.879	0.894	0.947	0.877	0.892	0.827	0.843
Cl	0.000		0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
OH	3.085		3.101	3.121	3.106	3.053	3.123	3.108	3.173	3.157
Sum anions	4.000		4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000

Notes: All Fe and Mn as FeO and MnO on the basis of spectroscopic information. *n* = number of individual analytical points used in the average.

^a Grand average of analysis over entire thin section.

^b Subset of grand average.

^c Second analysis of same general area.

^d Error in Li₂O and B₂O₃ measurements by nuclear microprobe analysis.

^e Total does not include B₂O₃meas. In accordance with the results of the structural refinement (*i.e.*, bond distances and site scatterings) and the nuclear reaction analysis, the B content can be assumed to be stoichiometric (B = 3 apfu). (OH) contents were calculated by stoichiometry.

The recorded optical spectra show considerable noise due to light scattering caused by microfractures in the thin absorbance wafer. Apart from a broad absorption band of low intensity at $\sim 23\,000\text{ cm}^{-1}$ in the E||a spectrum (Fig. 5) no additional bands are observed. This band is assigned to Fe²⁺–Ti⁴⁺ intervalence charge transfer processes (Taran *et al.*, 1993). Notably, the present spectra do not show the intensity enhanced absorption bands at $\sim 14\,000\text{ cm}^{-1}$ and $\sim 9000\text{ cm}^{-1}$

caused by Fe³⁺ intensity assisted Fe²⁺ *d*–*d* transitions that Mattson & Rossman (1987) recorded in spectra of tourmaline with mixed valence iron. This strongly supports the conclusion that iron is present as Fe²⁺. None of the typical intense Mn³⁺-bands in tourmaline (Reinitz & Rossman, 1988) were recorded in the present spectra. This, in combination with redox potential arguments, indicates that manganese occurs as Mn²⁺ in the present tourmaline.

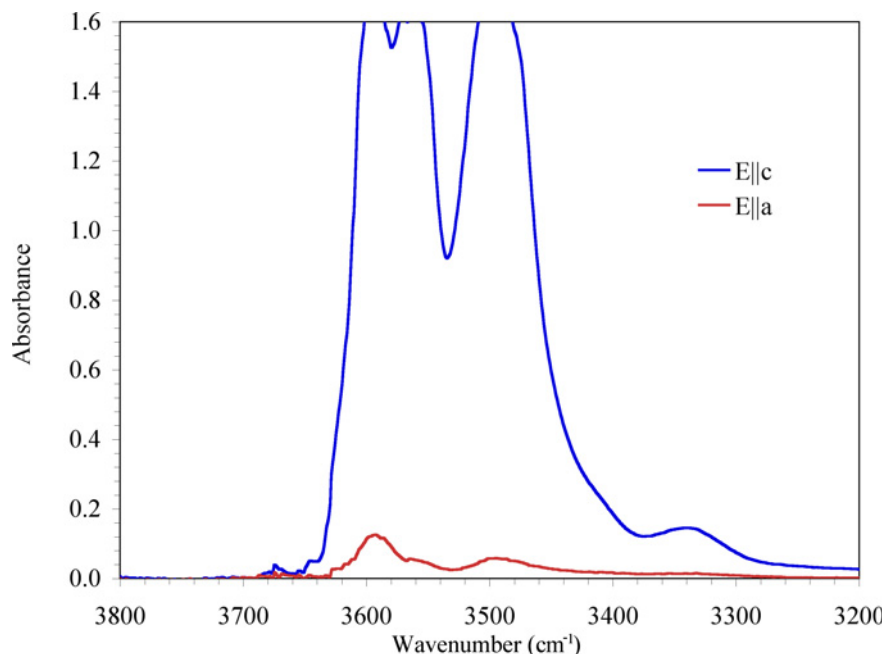


Fig. 4. Polarized single-crystal infrared spectra of fluor-elbaite in the O–H stretching region.

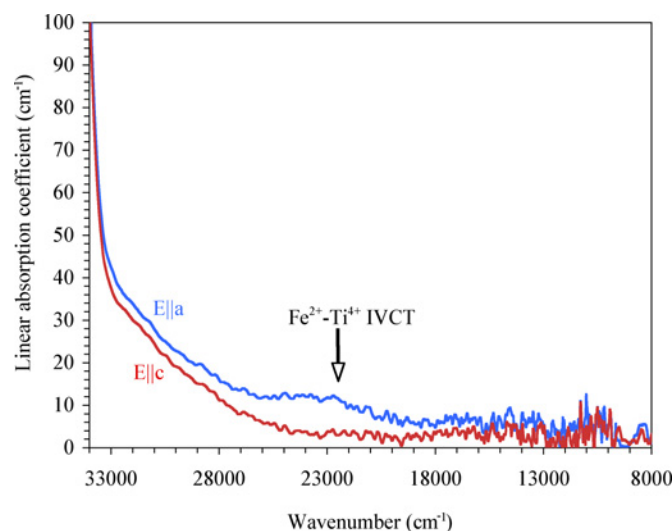


Fig. 5. Polarized single-crystal optical absorption spectra of fluor-elbaite.

4.2. Chemical composition of mica

Micas (Fig. 1) include lepidolite in flakes several millimeters across that are veined and overgrown by fine-grained muscovite (Fig. 2a and b); a few flakes are present in fluor-elbaite (Fig. 2c). The two compositional varieties of lepidolite, which contain *ca.* 8 wt% F (high-F) and *ca.* 6 wt% F (low-F), respectively (Table 5), are separated by a sharp boundary in back-scattered electron images (Fig. 2a). However, muscovite and the two varieties of lepidolite are each compositionally heterogeneous, and thus plots of major constituents *versus* fluorine show that the gaps in composition between muscovite and low-F lepidolite and

between low-F and high-F lepidolite do not greatly exceed compositional variation within muscovite and the two lepidolites (Figs. 3 and 6). The linear trend could be interpreted to result from interstratification of a Li- and F-free muscovite component and a lepidolite component composed of 35.2 wt% masutomilite, 52.8 wt% polyolithionite and 11.9 wt% trilithionite (see above). The fine layering revealed at high magnification (Fig. 2d) is consistent with this interpretation, but detailed X-ray or electron diffraction would be needed to confirm it.

Lithium contents calculated by our method ranged from 0.32 wt% to 1.46 wt% Li₂O in muscovite, 3.40–3.77 wt% Li₂O in low-F lepidolite and 4.53–5.18 wt% Li₂O in high-F lepidolite. For comparison, the regression

Table 5. Representative mica compositions.

Mica Location Spot no. <i>n</i>	Ms T. sect. 4 10	Ms Small 2 9	Ms Large 1a 8	Lpd T. sect. 2 10	Lpd Small 3 20	Lpd Small 6 20	Lpd Large 3 20	Lpd Large 4 20	Lpd Large 6 18
<i>wt%</i>									
SiO ₂	47.72	48.05	48.66	50.82	50.81	50.45	50.54	50.16	52.09
TiO ₂	0.01	0.00	0.00	0.03	0.01	0.01	0.00	0.00	0.00
Al ₂ O ₃	35.43	33.86	32.98	21.95	22.13	22.36	25.65	26.57	21.55
Cr ₂ O ₃	0.00	0.00	0.04	0.03	0.00	0.00	0.06	0.06	0.06
MgO	0.02	0.02	0.03	0.17	0.08	0.07	0.06	0.06	0.08
CaO	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00
MnO	0.66	0.80	0.96	2.70	2.91	2.80	1.85	1.78	2.68
FeO	0.91	1.25	1.34	2.76	2.79	2.66	2.00	1.94	2.53
BaO	0.01	0.02	0.08	0.00	0.02	0.01	0.09	0.09	0.11
Li ₂ Ocalc	0.36	0.91	1.36	4.83	5.03	4.88	3.77	3.40	5.18
Na ₂ O	0.22	0.16	0.17	0.13	0.14	0.11	0.23	0.22	0.12
K ₂ O	10.55	10.86	10.78	10.11	10.11	9.60	10.05	10.09	10.09
Rb ₂ O	n.a.	0.98	1.10	n.a.	n.a.	n.a.	1.55*	1.55*	1.38
Cs ₂ O	0.00	0.06	0.17	0.89	0.98	2.25	0.87	0.74	1.04
F	0.57	1.44	2.14	7.63	7.93	7.69	5.95	5.36	8.17
Cl	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
H ₂ Ocalc	4.29	3.87	3.56	0.79	0.67	0.76	1.67	1.95	0.61
O=F, Cl	−0.24	−0.61	−0.90	−3.21	−3.34	−3.24	−2.51	−2.26	−3.44
Total	100.51	101.66	102.45	99.62	100.28	100.41	101.84	101.72	102.24
<i>Formulae per 12 anions</i>									
Si	3.141	3.166	3.190	3.454	3.437	3.433	3.374	3.349	3.483
^{IV} Al	0.859	0.834	0.810	0.546	0.563	0.567	0.626	0.651	0.517
Sum IV	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Ti	0.001	0.000	0.000	0.002	0.001	0.001	0.000	0.000	0.000
^{VI} Al	1.890	1.795	1.737	1.212	1.202	1.226	1.392	1.440	1.181
Cr	0.000	0.000	0.002	0.001	0.000	0.000	0.003	0.003	0.003
Li	0.095	0.242	0.358	1.321	1.368	1.334	1.012	0.912	1.393
Mg	0.002	0.002	0.002	0.018	0.008	0.007	0.006	0.006	0.008
Mn	0.037	0.045	0.053	0.155	0.167	0.161	0.105	0.100	0.152
Fe	0.050	0.069	0.074	0.157	0.158	0.151	0.112	0.108	0.141
Sum VI	2.074	2.152	2.226	2.866	2.903	2.880	2.630	2.570	2.878
Na	0.029	0.020	0.022	0.017	0.018	0.014	0.029	0.029	0.015
K	0.886	0.913	0.901	0.876	0.873	0.833	0.856	0.860	0.860
Rb	—	0.042	0.046	—	—	—	0.066	0.066	0.059
Cs	0.000	0.002	0.005	0.026	0.028	0.065	0.025	0.021	0.030
Ca	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000
Ba	0.000	0.000	0.002	0.000	0.001	0.000	0.002	0.002	0.003
Sum XII	0.915	0.976	0.976	0.919	0.920	0.913	0.979	0.978	0.967
Total cations	6.989	7.129	7.201	7.785	7.823	7.793	7.609	7.548	7.845
F	0.118	0.300	0.444	1.640	1.697	1.655	1.256	1.132	1.728
Cl	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
OHcalc	1.881	1.700	1.556	0.360	0.303	0.344	0.744	0.868	0.272
Total anions	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

Notes: All Fe and Mn as FeO and MnO, respectively. n.a. — not analyzed, Ms — muscovite, Lpd — lepidolite. Locations: T. Sect. — thin section (Fig. 2c), large — large grain (Fig. 2a); small — small grain (Fig. 2b). *n* = number of individual analytical points used in the average.
* Single Rb measurement applied to two analytical spots.

recommended by Tischendorf *et al.* (1997) for muscovite, [di 1] gave 0.16–1.19 wt% Li₂O, whereas their recommended regression for lepidolite, [tri 1] gave 4.84–4.95 wt% Li₂O in low-F lepidolite and 4.92–5.42 wt% Li₂O in high-F lepidolite. In other words, regression [di 1], which is based solely on F content, gave lower F contents than our calculation for muscovite. Regression

[tri 1] based on SiO₂ content, gave comparable Li₂O content for high-F lepidolite, but markedly more Li₂O for low-F lepidolite compared to ours.

Lepidolite is noteworthy for its content of Cs₂O (0.7–2.25 wt%), whereas Cs₂O does not exceed 0.2 wt% in muscovite. In contrast, there is less difference in their Rb₂O contents, respectively 1.4–1.5 wt% and 1.0–1.1 wt%.

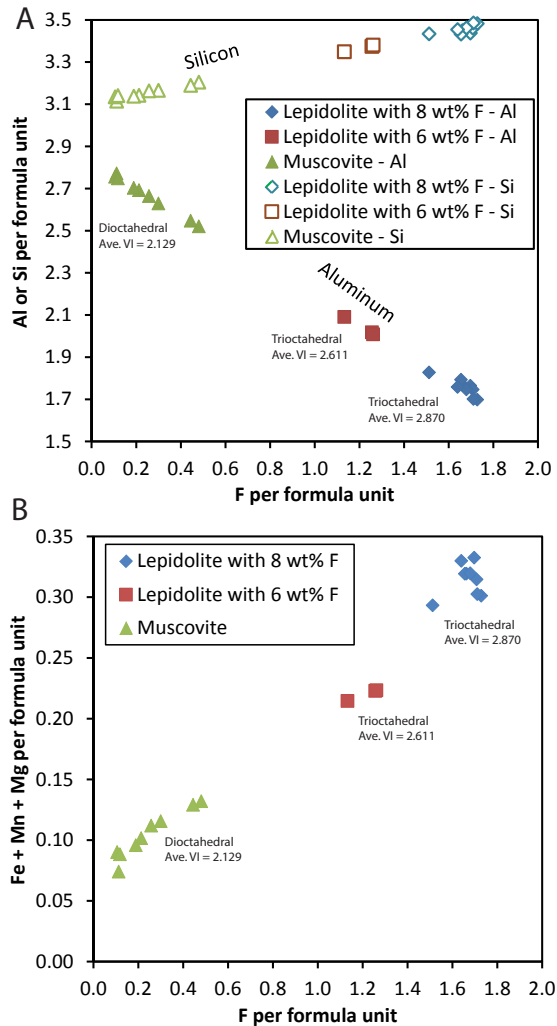


Fig. 6. Compositional variation in muscovite and lepidolite.

4.3. Chemical composition of spessartine and Ta–Nb oxides

Spessartine contains much subordinate amounts of grossular and almandine. Data of zones richest and poorest in MnO measured on one grain reveal minor heterogeneity (Table 6).

Oxides occur sparsely in muscovite, rarely in lepidolite, as grains up to 11 μm long. These dimensions are not sufficient to place the electron beam on the target grain without impinging matrix, so that analyses were contaminated with K_2O and Al_2O_3 (SiO_2 was not sought). Analyses were attempted on 6 grains, three of which gave totals of 93–98 wt% (Table 7). The formulae calculated for two of these grains correspond to fluorcalciomicrocline stoichiometry, $(\text{Ca}, \text{Na}, \square)_2(\text{Ta}, \text{Nb})_2\text{O}_6\text{F}$, except for F. The excess F in the formula could have been contributed by the mica matrix. The formula for a third grain corresponds closely to that for columbite-(Mn), $\text{Mn}^{2+}(\text{Nb}, \text{Ta})_2\text{O}_6$. Two other grains give WO_3 contents up to 39 wt% and MnO up to 12.5 wt% suggestive of hübnerite, whereas the sixth grain, which contains up to 4.5 wt% PbO, 3.5 wt% Nb_2O_5

Table 6. Composition of spessartine (one grain)

<i>n</i>	21	6
wt%		
SiO_2	36.88	36.65
TiO_2	0.01	0.01
Al_2O_3	20.77	20.73
Cr_2O_3	0.00	0.01
Y_2O_3	0.02	0.02
MgO	0.00	0.00
CaO	1.92	1.06
MnO	37.61	39.39
FeO	2.53	1.65
Sum	99.73	99.51
Formulae per 8 oxygen atoms		
Si	3.020	3.015
Ti	0.001	0.001
Al	2.004	2.010
Cr	0.000	0.000
Y	0.001	0.001
Mg	0.000	0.000
Ca	0.169	0.093
Mn	2.609	2.744
Fe	0.173	0.113
Sum	7.977	7.978
Components (mol%)		
Spessartine	88%	93%
Almandine	6%	4%
Grossular	6%	3%
Sum	100%	100%

Notes: All Fe and Mn as FeO and MnO, respectively. *n* = number of individual analytical points used in the average.

and 12.4 wt% Ta_2O_5 might be a Pb-bearing microlite, but contamination from surrounding mica precluded identifying the phase.

5. Origin of the pegmatite

The most noteworthy feature of the mineral assemblage in the Zishineni pegmatite is the presence of Li minerals (fluor-elbaite, lepidolite), significant Cs in lepidolite and Ta-bearing oxides, notably fluorcalciomicrocline, all features characteristic of the LCT (lithium–cesium–tantalum) family of pegmatites, which are most commonly associated with S-type granites (Černý & Ercit, 2005; Černý *et al.*, 2012; Hanson, 2016). Given ages of 2990 ± 43 Ma (Rb–Sr isochron, Trumbull, 1993) and 3074 ± 4 Ma (Pb–Pb zircon, Maphalala & Kröner, 1993) for the Sinceni Pluton, as well as the Rb–Sr minerals ages ranging from 2906 ± 31 Ma to 3072 ± 33 Ma for the pegmatites (Trumbull, 1993), the pegmatite is the first reported occurrence of a lithian tourmaline and lepidolite in the geologic record. Moreover, the Zishineni pegmatite and other pegmatites associated with the Sinceni granite are reported to be among the four geologically oldest rare-metal pegmatites worldwide, all *ca.* 3000–3100 Ma (Tkachev, 2011). In addition to the Sinceni pegmatites,

Table 7. Composition of oxides.

Mineral <i>n</i>	FCM 2	FCM 2	C-Mn 5
<i>wt%</i>			
WO ₃	0.80	0.46	1.64
Nb ₂ O ₅	5.82	7.04	37.35
Ta ₂ O ₅	65.07	61.63	34.01
TiO ₂	0.23	0.49	1.52
SnO ₂	2.72	2.71	0.25
Al ₂ O ₃	1.42	2.26	0.59
MgO	0.01	0.00	0.02
CaO	11.13	11.79	0.30
MnO	0.60	0.31	17.55
FeO	0.40	0.38	0.00
PbO	0.95	0.00	0.00
Na ₂ O	4.93	4.35	0.01
K ₂ O	0.80	0.74	0.11
F	5.31	4.80	0.00
O=F	−2.23	−2.02	0.00
Total	97.95	94.94	93.35
Oxygen	6.5	6.5	6.0
W	0.019	0.011	0.030
Nb	0.238	0.293	1.202
Ta	1.603	1.544	0.658
Ti	0.016	0.034	0.081
Sn	0.098	0.100	0.007
Sum	1.974	1.982	1.979
Mg	0.001	0.000	0.002
Mn	0.046	0.024	1.058
Fe	0.030	0.029	0
Sum	0.078	0.054	1.060
Ca	1.080	1.164	0.023
Pb	0.023	0	0
Na	0.865	0.777	0.001
Sum	1.968	1.942	0.024
Sum cations	4.019	3.977	3.062
F	1.520	1.400	0

Notes: All Fe as FeO. FCM – fluorcalciomicrocline, C-Mn – columbite-(Mn). K₂O and Al₂O₃ are not included in formulae calculations as these are likely contributed by the mica matrix.

two other groups are found in the Kaapvaal craton, namely pegmatites located in or near the Mpuluzi Batholith and pegmatites in the New Consort gold mines. The fourth locality is the Ivissartog area near Nuuk in southwestern Greenland. Pegmatites associated with the Mpuluzi Batholith contain cassiterite; only pegmatites associated with the Sinceni pegmatites contain Li or Ta minerals (Trumbull, 1995a; Maphalala & Trumbull, 1998; this study). The Greenland pegmatites contain beryl, but no Li minerals (Seacher *et al.*, 2008). Other than the Sinceni pegmatites, the only pegmatites *ca.* 3000–3100 Ma in age that clearly belong to the LCT family are reported in the New Consort gold mines along the northern flank of the Barberton greenstone belt: these pegmatites contain spodumene and show Cs enrichment, but not unusual Ta enrichment (Harris *et al.*, 1995).

Judging from its peraluminous chemical composition and mineralogy (tourmaline, muscovite) and from its initial ⁸⁷Sr/⁸⁶Sr ratio of 0.711, the Sinceni magma is most plausibly

derived from a metasedimentary source. Potential pelitic sediments of appropriate age can be found in the Pongola Supergroup which crop out in SW Swaziland (*e.g.*, Mukasa *et al.*, 2013). Most of the granitic batholiths and smaller plutons in the Barberton greenstone belt of South Africa and Swaziland are of I-type nature and belong to the so-called trondjemite-tonalite-granodiorite (TTG) suite, that dominates felsic magmatism in the Meso- and early Archean. The Sinceni granite and some of others of the so-called “younger granites” in Swaziland (ages 2.7–3.0 Ga) are different. In the context of tectonic environments that produce LCT pegmatites, Černý *et al.* (2012) noted that S-type granites such as Sinceni are typical for settings of crustal thickening associated with horizontal tectonic processes of subduction and continental collision. Martin & De Vito (2005) and Hanson (2016) also considered LCT pegmatites to be members of orogenic suites formed in subduction settings. If all S-type granites and related pegmatites formed in this way, the Sinceni LCT pegmatites could be taken as evidence for a collisional setting in the Mesoarchean. However, this is a simplistic view and Černý *et al.* (2012) cautioned that the main characteristics of the LCT pegmatites require only appropriate source rocks and heat source, irrespective of the tectonic regime. For example, geochemically similar tourmaline-topaz-beryl pegmatites and their parental S-type granite formed at about 130 Ma in the Erongo complex of Namibia (Trumbull *et al.*, 2008), in an anorogenic setting related to rifting and Gondwana breakup. We conclude that the Sinceni granite and pegmatites cannot be interpreted as evidence for plate tectonics in the Mesoarchean. Nonetheless, they do indicate that a “mature” (*i.e.* potassic, pelitic) continental crust existed in the Kaapvaal craton at *ca.* 3000 Ma, a time when much of the other Archean terranes were still composed of TTG series and greenstone belts.

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