

Tourmaline-group minerals from Norway, part II: Occurrences of luinaite-(OH) in Tvedalen, Larvik and Porsgrunn, and fluor-liddicoatite, fluor-elbaite and fluor-schorl at Ågskardet, Nordland

Uwe Kolitsch, Peter Andresen, Tomas Andersen Husdal, Andreas Ertl, Astrid Haugen, Hans Vidar Ellingsen & Alf Olav Larsen

Introduction

As part of a wider study on the crystal chemistry of tourmaline-group members from Norway, occurrences of luinaite-(OH), fluor-schorl and other members have been reported (Kolitsch et al. 2011). The present contribution presents further results based on characterisations of different samples from various pegmatite localities in the Langesundsfjord area (Tvedalen, Larvik, Porsgrunn), in Østfold, Nordland, Oppland and Telemark. The Langesundsfjord samples also include material described by Brøgger (1890). The following species were detected: schorl, fluor-schorl, luinaite-(OH), "luinaite-(F)", dravite, fluor-elbaite, fluor-liddicoatite and rossmanite. Additionally, bastnäsite-(La) and cassiterite were detected as unexpected inclusions in a polished section of a Langesundsfjord schorl sample.

As in our previous study the chemical compositions of the samples have been derived from a combination of single-crystal structure refinements and semiquantitative SEM-EDS analyses (Kolitsch et al. 2011, see there for additional details). The refinements were again done using intensity data collected at ambient temperature on a Nonius KappaCCD single-crystal X-ray diffractometer equipped with a CCD detector. The SXRD data were collected from selected crystal fragments with high crystal quality (a common case for tourmaline-group species) and average diameters between about 0.1 and 0.2 mm. For all samples, intensity data were measured with high redundancy for a complete Ewald sphere up to $2\theta = 75^\circ$, ensuring high-resolution data sets and good statistics. The data were processed in a standard way, with absorption correction based on the multi-scan method. Final $R(F)$ values usually ranged between around 1 and 2%. Since an accurate determination of the F:(OH,O) ratio at the W site can be achieved very easily from such high-quality datasets, it was consequently easy to distinguish between F- and OH-dominant members of the tourmaline group.

From the refined crystal-structure model, the chemical formula of a given sample was indirectly estimated by means of numerous well-established relations between unit-cell parameters, bond lengths, site occupancies and polyhedral geometries in the tourmaline group, as well as bond-valence constraints (e.g. Ertl et al. 2001 & 2002, Hawthorne 2002, Bosi & Lucchesi 2004, Ertl & Tillmanns 2010, Ertl et al. 2010, Henry & Dutrow 2011, Henry et al. 2011, Ertl & Tillmanns 2012). This correlation-based identification method only fails if a given tourmaline sample is very or fairly near the compositional boundary between two or more species. In such cases, quantitative EPMA data will be necessary, in part to be supplemented by SIMS or wet-chemical analyses for Li and determination of the accurate $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio by Mössbauer spectroscopy.

For the SEM-EDS analyses at the Natural History Museum Vienna, a new, state-of-the-art JEOL JSM-6610LV equipped with a high-resolution and high-sensitivity detector (e-FlashHR+; detector area 30 mm², resolution 127 eV) was employed. The data, obtained on carbon-coated samples (either polished sections or flat-lying fragments), were processed by Bruker Esprit 1.9.4 software, using an interactive PB-ZAF correction for the semi-quantitative analyses. This allowed surprisingly accurate determination of all non-oxygen and -hydrogen element constituents, including F (only F contents < 0.2-0.3 apfu are seemingly below the detection limit). Similarly to our previous study (Kolitsch et al. 2011), the largest variation within a given set of analysed fragments from the same sample was shown by the Al:Fe:Mg ratios.

Results from the SEM-EDS analyses all agree well with the results of the crystal-structure refinements and the derived structure models.

Samples and localities

The following sample descriptions are arranged in a geographical order. First, the tourmalines from the Langesundsfjord area (Vestfold and Telemark) are described, followed by those from Østfold, Nordland, Oppland and Telemark.

Previously, only schorl was reported from the wider Langesundsfjord area (Brøgger 1890, Larsen et al. 1999, Larsen 2010). The blackish, prismatic crystals have crystallised in the hydrothermal stage of the nepheline syenite pegmatites, and are generally embedded in analcime. The prisms may reach a length of 5 cm and are often arranged in divergent groups (Larsen 2010).

Midtjfellet quarry, Malerød, Larvik, Vestfold

Two samples from this operating larvikite quarry were studied. The first one (collected in 2007 by PA) shows a brown-black, radiating tourmaline (Fig. 1) embedded in an analcime/spreustein-type natrolite matrix, with minor pale blue sodalite and trace amounts of zircon and other minerals. Dark chlorite occurs in analcime voids.

The SXRD study clearly shows this sample to be luinaite-(OH) (IMA 2009-046). We remind that luinaite-(OH) is a monoclinic-pseudorhombic member of the tourmaline group, and has the simplified formula $(\text{Na}, \square)(\text{Fe}^{2+}, \text{Mg})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$. The decrease in space-group symmetry from *R3m* (rhombohedral) to *Cm* (monoclinic) is caused by an ordering of Fe³⁺ and Al³⁺ cations which appears to be governed by the conditions of crystallisation (Mills et al., to be submitted).

The ordering is strongly pronounced at the Y site, less so at the Z site. The Y1O₆ polyhedron is unusual because it shows a very strong bond-length distortion (range: 1.925(2) - 2.1632(18) Å), unlike the Y2O₆ polyhedron (range: 2.0269(11)- 2.1877(12) Å). The refined occupancies of the Y1 and Y2 sites are Fe_{0.593(4)}Al_{0.407(4)} and Fe_{0.803(3)}Al_{0.197(3)}, respectively. Further details will be reported in the original description of luinaite-(OH) (Mills et al., to be submitted).

The only impurity element detected by SEM-EDS is Ti in trace amounts.

Refined unit-cell parameters: $a = 10.453(2)$, $b = 16.013(3)$, $c = 7.232(1)$ Å, $\beta = 117.64(3)^\circ$.
Refined chemical formula (bulk formula, occupancies of individual split Y and Z sites not indicated): $\sim(\text{Na}_{0.98}\text{Ca}_{0.02})(\text{Fe}_{0.70}\text{Al}_{0.30})_3(\text{Al}_{0.89}\text{Fe}_{0.11})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.8}\text{F}_{0.2})$.

quarry. The first one (collected by AOL) showed a spray of dark prisms up to ca. 2.5 cm (!) in length, embedded in white nepheline syenite pegmatite matrix (Fig. 4). The larger prisms appear black, while the smaller ones show a dark brownish colour. SEM-EDS analyses evidence minor Mg (Fe:Mg ~ 6:1 to 10:1) and trace amounts of Mn and Ti.

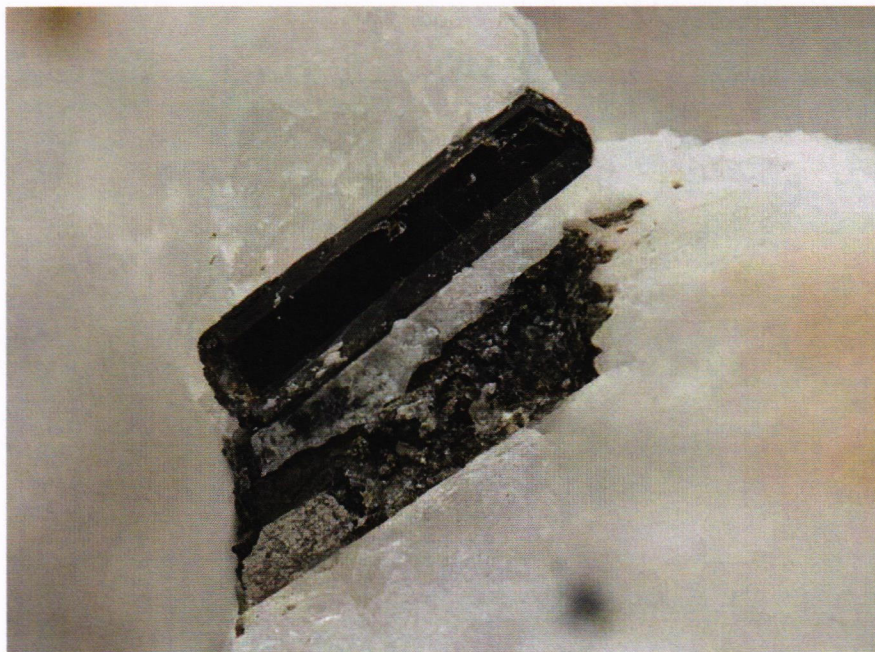


Fig. 3. Two prismatic crystals of luinaite-(OH) from level 4 of the AS Granit quarry, Tuften, Tvedalen, Larvik, Vestfold. Note that the broken lower crystal is hollow and filled with tiny analcime crystals. Field of view 4.8 mm. Photo Harald Schillhammer.



Fig. 4. A large spray of F-bearing schorl from Almenningen quarry, Tvedalen, Larvik, Vestfold. Field of view 2.9 cm. Photo Harald Schillhammer.

The second sample (collected by PA) consisted of a small part of a spray of black prisms in white nepheline syenite pegmatite matrix (Fig. 5). SEM-EDS analyses reflect a fairly homogeneous composition characterised by a minor amount of Mg (Fe:Mg ~ 5:1) and trace amounts of Mn and Ti. The Ca or F contents were below the detection limit, although the refinements of both samples clearly indicated very small amounts of both these elements at the X and W sites, respectively.

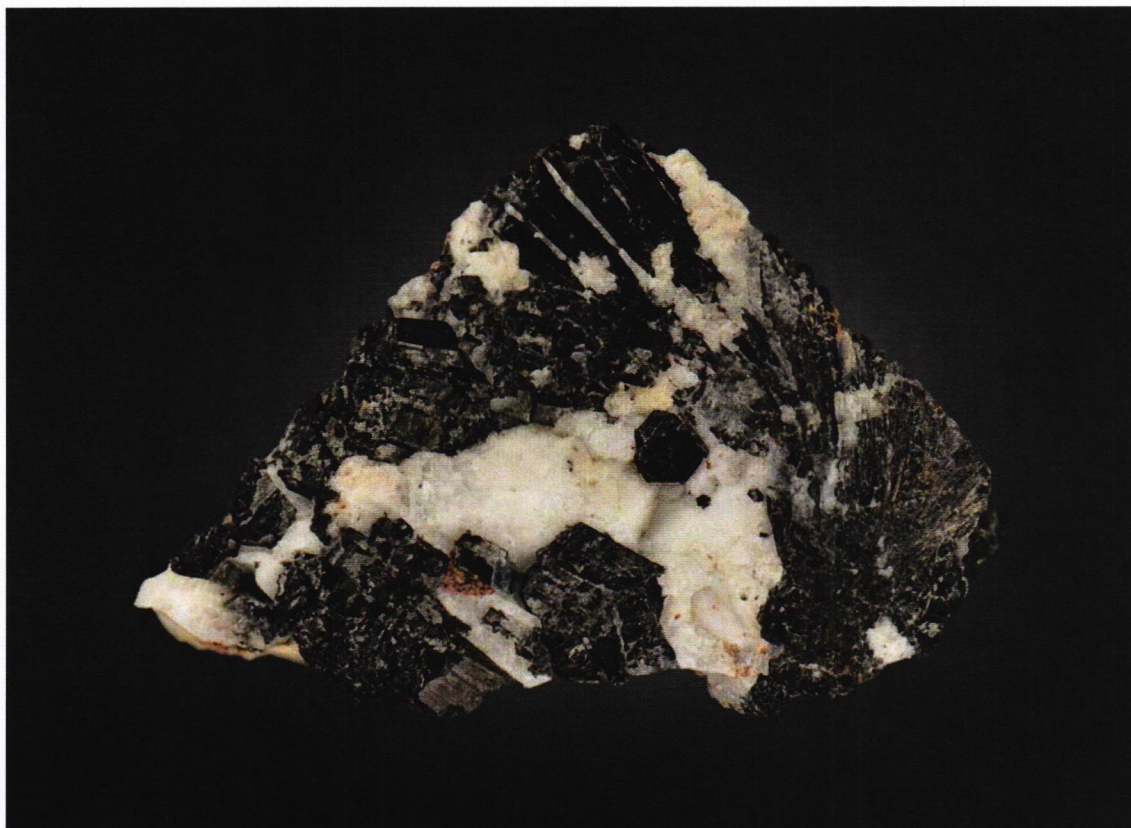


Fig. 5. F-bearing schorl from Almenningen quarry, Tvedalen, Larvik, Vestfold. This sample contains inclusions of thorite, xenotime-(Y), bastnäsite-(La), cassiterite and others (see text and Figs. 6-11). Field of view 1.8 cm. Photo Harald Schillhammer.

Since the studies gave very similar unit-cell parameters and chemical compositions for both samples, the results will be described together. The two samples are both F-bearing schorl which showed no indication of lower (monoclinic) symmetry.

Refined unit-cell parameters: $a = 16.004(2)$, $c = 7.233(1)$ Å (AOL sample).

$a = 16.011(2)$, $c = 7.231(1)$ Å (PA sample).

Refined chemical formulae:

$\sim(\text{Na}_{0.98}\text{Ca}_{0.02})(\text{Fe}_{0.65}\text{Mg}_{0.15}\text{Al}_{0.20})_3(\text{Al}_{0.88}\text{Fe}_{0.12})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.8}\text{F}_{0.2})$ (AOL sample).

$\sim(\text{Na}_{0.98}\text{Ca}_{0.02})(\text{Fe}_{0.66}\text{Mg}_{0.15}\text{Al}_{0.19})_3(\text{Al}_{0.90}\text{Fe}_{0.10})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.6}\text{F}_{0.4})$ (PA sample).

The overall features of the two samples are also very similar to that of a schorl from the Østskoggen quarry (see following description).

SEM-EDS analyses of a polished section of the second sample revealed a surprising wealth of inclusions (in either analcime or, less commonly, schorl) and secondary phases (in tiny voids or crack fillings). The dominant inclusion is thorite (an- to euhedral, up to ~100 µm) that

is generally highly inhomogeneous. As minor impurity elements Ca, Mn, Fe, Y, Na, F and trace amounts of Pb, U and P were observed, all in variable percentages. In near-end member thorite the only foreign elements were Y and P. An unidentified phase always concentrated at the rim of the thorite grains, which contains additional Nb and more Fe, Mn and/or Al, but less Th, seems to be an alteration phase and a mixture of different species. The second most common inclusion is xenotime-(Y) (mostly euhedral; sometimes in the core of thorite grains; Yb-, Er-, Dy- and Al-bearing; Fig. 6), followed by zircon (Hf-bearing, with Zr:Hf ~ 10:1). Very rare is cassiterite found as tiny (max. 5 µm), anhedral inclusions (Figs. 7, 8). The only observed impurity element was Fe in trace quantities. Cassiterite was a previously unknown component of the Langsundsfjord pegmatites. A further unidentified phase forming a larger grain featuring a system of mutually perpendicular cracks conforms a Ce silicate with minor Mn, Al, Ca, Y, Na and trace amounts of Pb and Ce. The ratio (Ce + metals):Si is around 2:1. Possibly this grain is tritomite-(Ce).

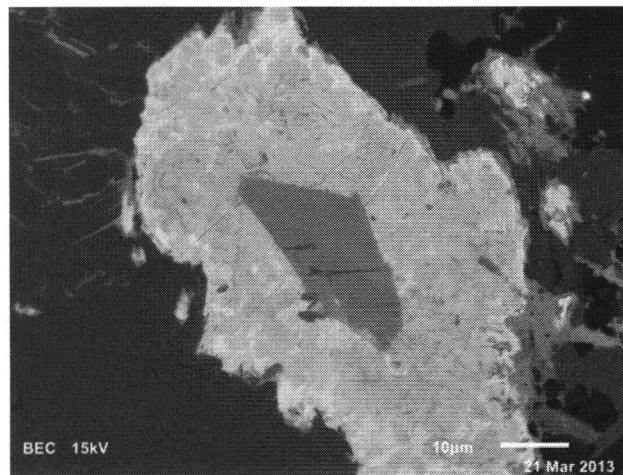


Fig. 6. Zoned xenotime-(Y) (the brighter areas contain more Yb) in the core of an inhomogeneous thorite, as inclusions in a sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.

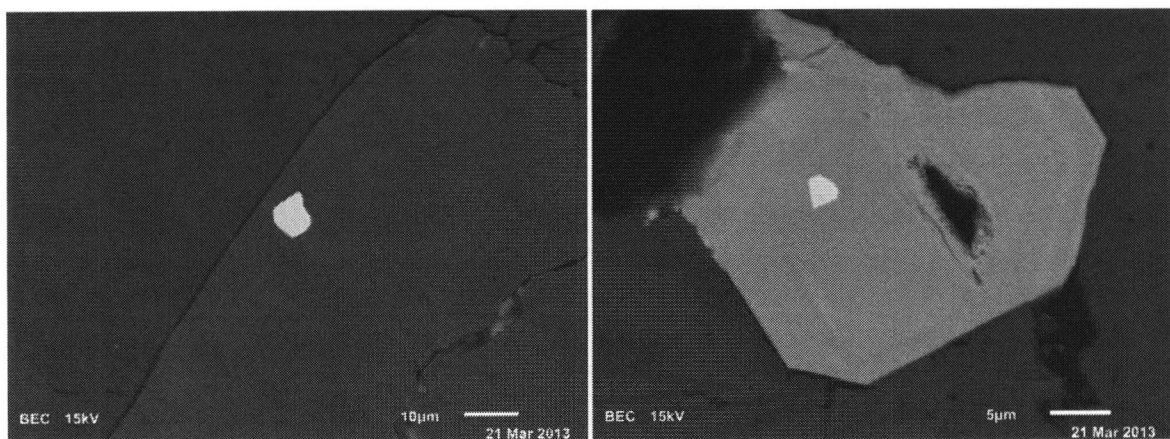


Fig. 7 (left). Tiny cassiterite grain (bright) in schorl, next to analcime (darker), in a sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.

Fig. 8 (right). Tiny cassiterite grain (bright) within a zoned xenotime-(Y), in a sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.

Further inclusions were near-stoichiometric annite, chamosite (Fe:Mg ~ 10:1; some with elevated Zn contents), very rare pyrophanite (containing trace amounts of Nb) and an aluminosilicate clay (Al:Si ~ 1:1) with trace amounts of Na and Ca. Among the secondary phases, bastnäsite-(La) is dominant, followed by bastnäsite-(Ce). Both form tiny rounded platelets, either arranged in sprays embedded in matrix or as crusts covering surfaces of tiny voids (Figs. 9-11). They contain variable to trace amounts of (in decreasing order) Nd, Y, Ca, Pr, Na, Fe, Nb(!), Pb, Th, Al(?) and Si(?). Some bastnäsite-(La) is completely free of Ce and thus indicates a prior complete oxidation of the Ce^{3+} to Ce^{4+} , which then precipitates as CeO_2 and is removed from the mineralising solutions (a typical phenomenon during the alteration of primary LREE-bearing phases). Other bastnäsite-(La) aggregates are characterised by increased Ce contents, with La:Ce up to approximately 2:1 or even 1:1. Bastnäsite-(Ce) itself is less common and always La-rich (Ce:La ~ 3:2). The analytically determined F contents of the bastnäsites clearly indicate F-dominance, although some spot analyses also suggest decreased F contents and therefore an increased hydroxylbastnäsite-(La/Ce) component. Only quantitative EPMA would be able to prove if some aggregates actually correspond to F-bearing hydroxylbastnäsite-(La/Ce). Bastnäsite-(La) appears to be a new find for Norway. Ce-free hydroxylbastnäsite-(La) was analysed in a sample from Tuften, Tvedalen (Pavel M. Kartashov, unpubl. results; see <http://www.mindat.org/photo-415857.html>).

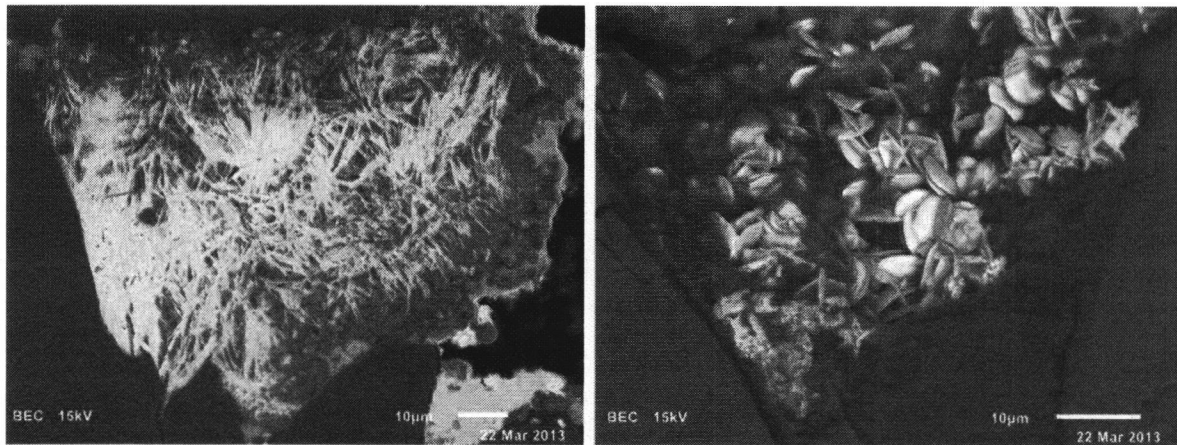


Fig. 9 (left). Fibrous, Ce-rich bastnäsite-(La), in a sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.
Fig. 10 (right). Bastnäsite-(La) as tiny rounded platelets, in a void in a sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.

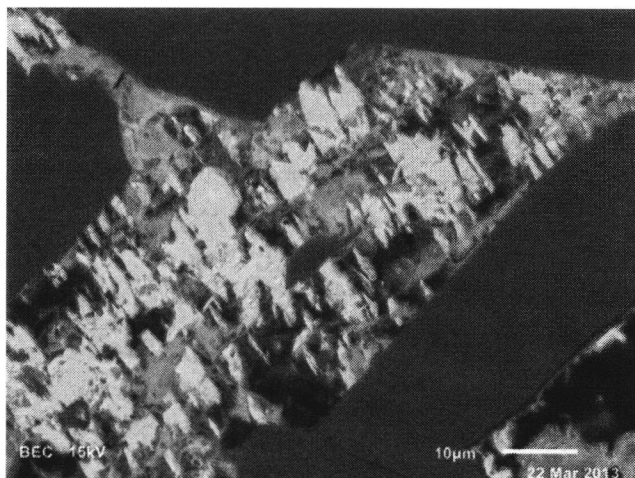


Fig. 11. Bastnäsite-(La) as bright parallel lamellae, associated with an unidentified phase (bright grey) containing Ce, Si, Al and various other elements. The dark matrix is schorl. Sample of F-bearing schorl from Almenningen quarry (polished section). SEM micrograph (BSE mode) Uwe Kolitsch.