

New crystal-chemical data for members of the tourmaline group from Norway: occurrences of fluor-schorl and luinaite-(OH)

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Introduction

Recently three new members of the tourmaline group, fluor-schorl (IMA 2010-067), fluor-dravite (IMA 2009-089) and luinaite-(OH) (IMA 2009-046), have been identified and approved by the CNMNC-IMA, and a revised nomenclature of the tourmaline group has been established (Henry et al. 2011). Two of the authors (UK and AE) were involved in the descriptions of fluor-schorl and luinaite-(OH), and we are also working on the description of a presently unnamed F-analogue of luinaite-(OH), identified from a German locality.

The first of the three new species, fluor-schorl, $\text{NaFe}^{2+}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{F}$, is the F-analogue of schorl [$\text{NaFe}^{2+}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$], and occurs in F-rich environments encountered in pegmatites and hydrothermal veins (Ertl et al., to be submitted). It has already been known (from quantitative chemical analyses) for quite some time from a fairly large number of worldwide localities (cf. Henry & Dutrow 2011), but only a detailed crystal-structure refinement of a sample from South Tyrol with a near-endmember composition (Ertl et al. 2006), in combination with a full chemical analysis, finally led to a complete characterisation of the mineral (Ertl et al., to be submitted). The type locality is twofold: Alluvial tin deposits near Steinberg, Zschorlau, Erzgebirge, Saxony, Germany, and pegmatites at Grassein, Trentino, South Tyrol, Italy.

The second new species, fluor-dravite, $\text{NaMg}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{F}$, is the F-analogue of dravite [$\text{NaMg}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$]. Its type locality is the Crabtree emerald mine, North Carolina, USA, where it occurs at the boundary of a small body of granitic pegmatite with the surrounding country-rock. The original description of fluor-dravite was published by Clark et al. (2011). Literature data on chemical compositions of F-dominant "dravites" suggests that a considerable number of additional occurrences exist (Henry & Dutrow 2011).

Luinaite-(OH) is a monoclinic-pseudorhombohedral 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 Fe^{3+} and Al^{3+} cations which appears to be governed by the conditions of crystallisation (Mills et al., to be submitted).

The lowering of symmetry in samples of the tourmaline group has previously been reported in the literature. Akizuki et al. (2001) described triclinic, orthorhombic and rhombohedral domains in single crystals of liddicoatite and elbaite from Madagascar. Shtukenberg et al. (2007) reported biaxial elbaite-liddicoatite from Russia and also inferred triclinic symmetry for their sample. The cause for the triclinic-pseudorhombohedral symmetry was attributed to the ordering of Li^+ and Al^{3+} cations by a growth dissymmetrisation mechanism. Very recently, Hughes et al. (2011) provided data for a sectorally zoned triclinic Ni-bearing dravite from the Berezovskoe gold deposit, Russia.

All three species may only be identified by accurate determination of the chemical composition and crystallography, preferably by a combination of single-crystal X-ray structure

refinements and chemical analyses. Specifically, a correct identification of luinaite-(OH) requires high-resolution crystal structure refinements.

The above identifications have prompted us to (re-)study tourmalines from a selection of Norwegian occurrences, since a certain number of pegmatites in Norway are known for their richness in primary and secondary fluorides and F-bearing minerals (e.g. those in the Tysfjord area, Husdal 2008).

A previous study of 52 selected tourmalines from Norway (Larsen et al. 1999) used partial chemical analyses (EPMA and XRF data; Li, B and H not measured) for the characterisation, although a determination of the F content was presented only for a small minority of the studied samples. The only F-dominant (on the *W* site) sample was an olive-green liddicoatite from Sandnessjøen (no. 43).

Distinguishing between F- and OH-dominant members of the tourmaline group can be done relatively easily by means of an accurate determination of the F:(OH,O) ratio on the *W* site, the only site in the tourmaline structure which can be occupied by F⁻ anions. Fortunately, this ratio can be reliably refined, if high-quality single-crystal X-ray diffraction data are available (Ertl & Kolitsch, unpublished results based on studies of numerous tourmaline samples). From a crystal-structure refinement it is also fairly easy to indirectly estimate the complete chemical composition of a given sample by means of 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, Henry & Dutrow 2011). 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 Mössbauer spectroscopic studies of the accurate Fe³⁺:Fe²⁺ ratio.

The following samples were studied using semiquantitative SEM-EDS analyses and single-crystal X-ray structure refinements of intensity data collected at ambient temperature on a Nonius KappaCCD single-crystal X-ray diffractometer equipped with a CCD detector. The 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. The data were processed in a standard way, with absorption correction based on the multi-scan method. Final $R(F)$ values usually ranged between 1 and 2%.

The SEM-EDS analyses proved to be fairly sensitive. The F peak in all strongly F-dominant samples was clearly visible in the spectrum, although F represents only one atom out of 50 non-hydrogen atoms in the general chemical formulae of F-dominant species in the tourmaline group. The largest variation within a given set of analysed fragments from the same sample was shown by the Al:Fe ratio, except for the Lindvikskollen sample in which the Fe:Mg ratio varied strongly. Results from the SEM-EDS analyses were all in good agreement with the crystal-structure refinements.

The present contribution presents the current results of a study which is not fully completed yet. Specifically, it is planned to conduct quantitative EMP analyses and Raman spectroscopic measurements for some of the more interesting samples, and to study more samples.

Samples and localities

Hundholmen, Tysfjord, Nordland

Hundholmen is a NYF-pegmatite with abundant fluorite, both "normal" and the Y-bearing variety "yttrofluorite" (associated with rich REE-mineralization). The two studied samples, however, originate from a seemingly F-poor paragenesis: a crack in feldspar with albite, calcite, muscovite and quartz as dominant phases. The mineralogy of the pegmatite is described in detail by Husdal (2008). A view of the locality is given in Fig. 1.

The first sample was a small aggregate of subparallel, black, hydrothermally corroded (in part hollow) prisms, partly overgrown with globular chamosite (Mg-free according to SEM-EDS analyses) and very minor calcite; it is shown in Figs. 2 and 3. Processing of the dataset clearly suggested that this tourmaline was monoclinic (space group *Cm*) and not rhombohedral. This was subsequently confirmed by crystal-structure refinements that also showed that the sample is OH-dominant on the *W* site, and therefore luinaite-(OH).

Refined unit-cell parameters: $a = 10.433(2)$, $b = 16.045(3)$, $c = 7.241(1)$ Å, $\beta = 117.61(3)^\circ$.

Refined chemical formula (bulk formula, occupancies of individual split Y and Z sites not indicated): $\sim(\text{Na}_{0.94}\square_{0.06})(\text{Fe}_{0.74}\text{Al}_{0.26})_3(\text{Al}_{0.85}\text{Fe}_{0.15})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.8}\text{F}_{0.2})$.

The second sample consisted of thin dark (black-brown), subparallel prisms, overgrown by thin grey-green chamosite crust and late massive calcite. Although this sample was visually similar to the first one, the data processing and the crystal-structure refinements nonetheless demonstrated that it is rhombohedral within error limits (and not monoclinic as the first one), but otherwise has a similar chemical composition, again with a clear OH-dominance on the *W* site. Therefore, it is a schorl.

Refined unit-cell parameters: $a = 16.015(2)$, $c = 7.227(1)$ Å.

Refined chemical formula:

$\sim(\text{Na}_{0.81}\square_{0.19})(\text{Fe}_{0.68}\text{Al}_{0.32})_3(\text{Al}_{0.87}\text{Fe}_{0.13})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.7}\text{F}_{0.3})$.

The very high Fe-for-Al substitution on the Z site of both samples, ($\text{Al}_{0.85}\text{Fe}_{0.15}$) and ($\text{Al}_{0.87}\text{Fe}_{0.13}$), respectively, is noteworthy.

SEM-EDS analyses of both samples showed only Na, Fe, Al, Si and O. EDS spectra of similar "schorl" crystals from Hundholmen also showed no Mg at all, only Na, Fe, Al, Si and O.

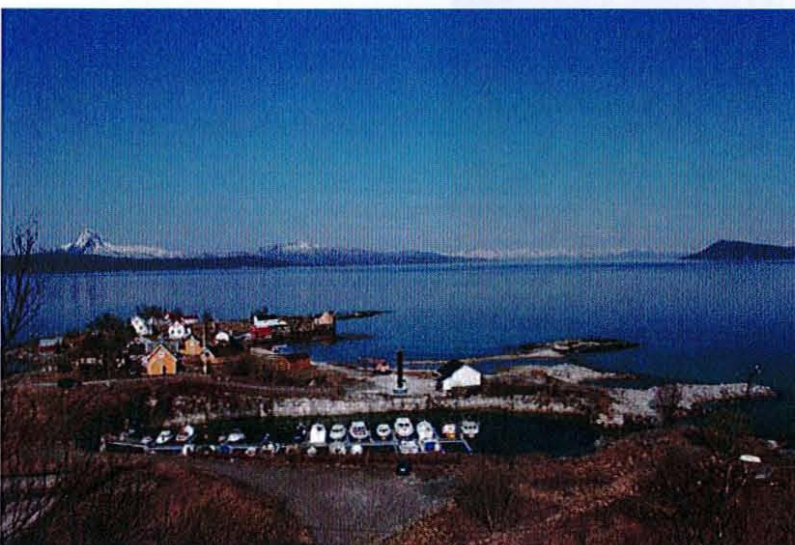


Fig. 1. Panoramic view of the Hundholmen locality: remnants of dumps with pegmatite material on the shore. Photo TAH.



Fig. 2. The inconspicuous luinaite-(OH) from Hundholmen: subparallel, black, hydrothermally corroded (partly hollow) prisms, locally overgrown with globular brownish chamosite and very minor calcite (white). Photo Fritz Schreiber.



Fig. 3. Close-up view of the large sample containing both luinaite-(OH) and schorl from Hundholmen. Photo TAH.

Tennvatn, Sørfold, Nordland

Several samples from this amazonite pegmatite were collected by TAH and two of them were studied for the present contribution (a typical black tourmaline in situ is shown in Fig. 4). The first sample, consisting of brown-black grains, turned out to be a F-dominant (very F-rich), Al-rich tourmaline, i.e., a fluor-schorl. SEM-EDS analyses showed Na, Fe, Al, Si, O and F, as well as traces of Mn and Ti, but no Mg.

Refined unit-cell parameters: $a = 15.989(2)$, $c = 7.167(1)$ Å.

Refined chemical formula: $\sim(\text{Na}_{0.91}\square_{0.09})(\text{Fe}_{0.56}\text{Al}_{0.44})_3(\text{Al}_{0.96}\text{Fe}_{0.04})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{F}_{0.9}\text{OH}_{0.1})$.

The second sample consisted of several small fragments with dark brown to blackish brown prisms in quartz and white feldspar. The structure refinement showed that it is very similar to the first sample, and also a fluor-schorl. The SEM-EDS spectra were very similar to those of the first sample.

Refined unit-cell parameters: $a = 15.990(2)$, $c = 7.166(1)$ Å.

Refined chemical formula: $\sim(\text{Na}_{0.92}\square_{0.08})(\text{Fe}_{0.58}\text{Al}_{0.42})_3(\text{Al}_{0.96}\text{Fe}_{0.04})_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{F}_{0.9}\text{OH}_{0.1})$.

The high Na content on the X site is in good agreement with the strong F-dominance on the W site, a correlation recently confirmed by Henry & Dutrow (2011).

A black tourmaline sample from Tennvatn was previously studied by Larsen et al. (1999) using XRF analysis. This sample was extremely Fe-rich and had a bulk composition $(\text{Na}_{0.89}\text{K}_{0.02}\text{Ca}_{0.02}\square_{0.07})(\text{Fe}_{0.96}\text{Ti}_{0.03}\text{Mn}_{0.02}\text{Mg}_{0.01}\text{Zn}_{0.01})_{3.03}(\text{Al}_{0.98}\text{Fe}_{0.02})_6(\text{Si}_{0.98}\text{Al}_{0.02})_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$, i.e. close to that of the schorl end-member. However, since the F content was not determined, it might actually have been a fluor-schorl.

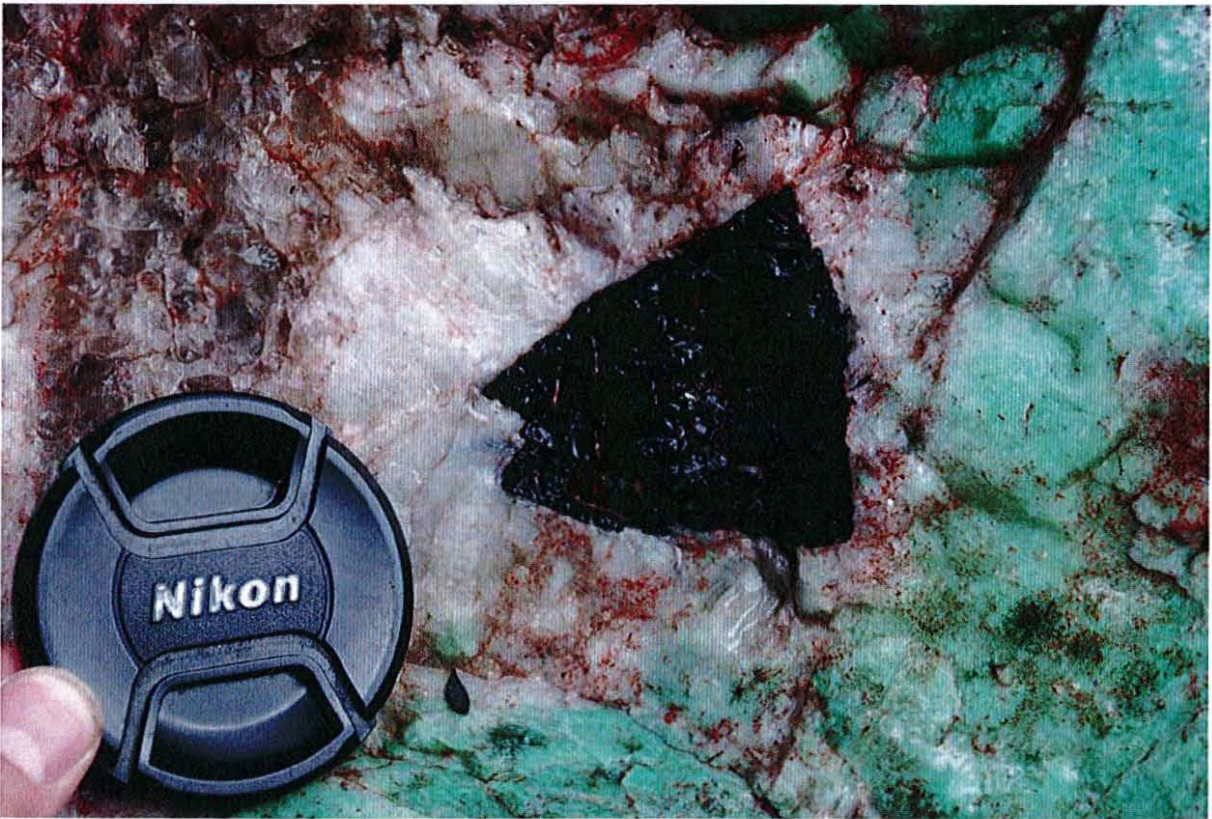


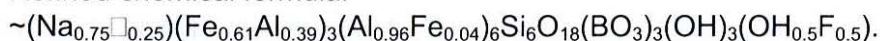
Fig. 4. Large black tourmaline crystal (cross-section) in situ within pegmatite matrix from Tennvatn. Two typical samples were both identified as fluor-schorl. Photo TAH.

Ågskardet, Holandsfjord, Meløy, Nordland

This sample was collected by TAH in 2002. It consists of black prisms in white feldspar and pale grey quartz. The locality is an el baite-rich LCT-pegmatite. The structure studies demonstrates that the sample is a F-rich (OH:F ~ 1:1), Al-rich schorl. Only quantitative EPMA would show if parts of the crystal show a distinct F-dominance or not. SEM-EDS analyses showed Na, Fe, Al, Si, O and trace amounts of Mg.

Refined unit-cell parameters: $a = 15.987(2)$, $c = 7.173(1)$ Å.

Refined chemical formula:



Kjøpsvik, Tysfjord, Nordland

Kjøpsvik is a large active quarry in Caledonian marble. This quarry is known for a smaller number of minerals, as well as fluorite and brown "dravite" tourmalines in matrix or in calcite voids (Tomas A. Husdal, unpublished results; see <http://www.mindat.org/loc-144241.html> for list of presently known minerals from this locality). The occurrence of fluorite in a similar assemblage as that of the tourmaline suggested to us that the latter could actually be a F-dominant species. A representative sample was therefore studied. The sample, collected by TAH, was a small, fractured pale brownish crystal half-embedded in calcite crystals. The structure refinement demonstrated that the sample was a very F-rich, Ca-bearing dravite (with very low Fe content) that in fact may be F-dominant. According to the refined model, the occupancy of the *W* site is (F_{0.6}OH_{0.4}). However, the estimated real error is +/- 0.1 for these values and therefore quantitative chemical analysis (EPMA) will be necessary for a final assignment of this sample to either F-rich dravite or OH-rich fluor-dravite. SEM-EDS analyses confirmed the very low Fe content and also the presence of Ca replacing approximately half of the Na.

Refined unit-cell parameters: $a = 15.955(2)$, $c = 7.199(1)$ Å.

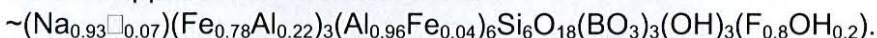
Refined chemical formula: $\sim(\text{Na}_{0.55}\text{Ca}_{0.30}\square_{0.15})(\text{Mg}_{0.97}\text{Fe}_{0.03})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{F}_{0.6}\text{OH}_{0.4}).$

Kjerstadjellet, Tjeldsund, Nordland

The mineralogy of this pegmatite is similar to that of the Tennvatn pegmatite. The sample consisted of black prisms and was collected by TAH in 2003. The structure refinement shows that this sample can be assigned to a very Fe-rich fluor-schorl (refined F:O ratio = 0.8:0.2). SEM-EDS analyses showed Na, Fe, Al, Si, O, F and traces of Ti.

Refined unit-cell parameters: $a = 16.025(2)$, $c = 7.196(1)$ Å.

Refined approximate chemical formula:



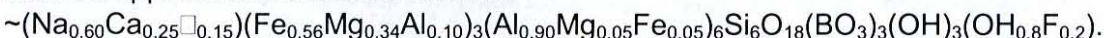
Lindvikskollen. Kragerø, Telemark

The sample, thin dark (black-brown), subparallel prisms in pale smokey quartz (Fig. 5), was collected by the first author in 1988 from the Lindvikskollen NYF-pegmatite, a classical locality in Norway.

The structure refinement indicated the sample to be a Ca-, Al- and Mg-rich schorl containing minor F. This was confirmed by SEM-EDS analyses that showed Na, Fe, Mg, Al, Si, O and minor Ca (with Na:Ca ~ 2:1).

Refined unit-cell parameters: $a = 16.005(2)$, $c = 7.227(1)$ Å.

Refined approximate chemical formula:



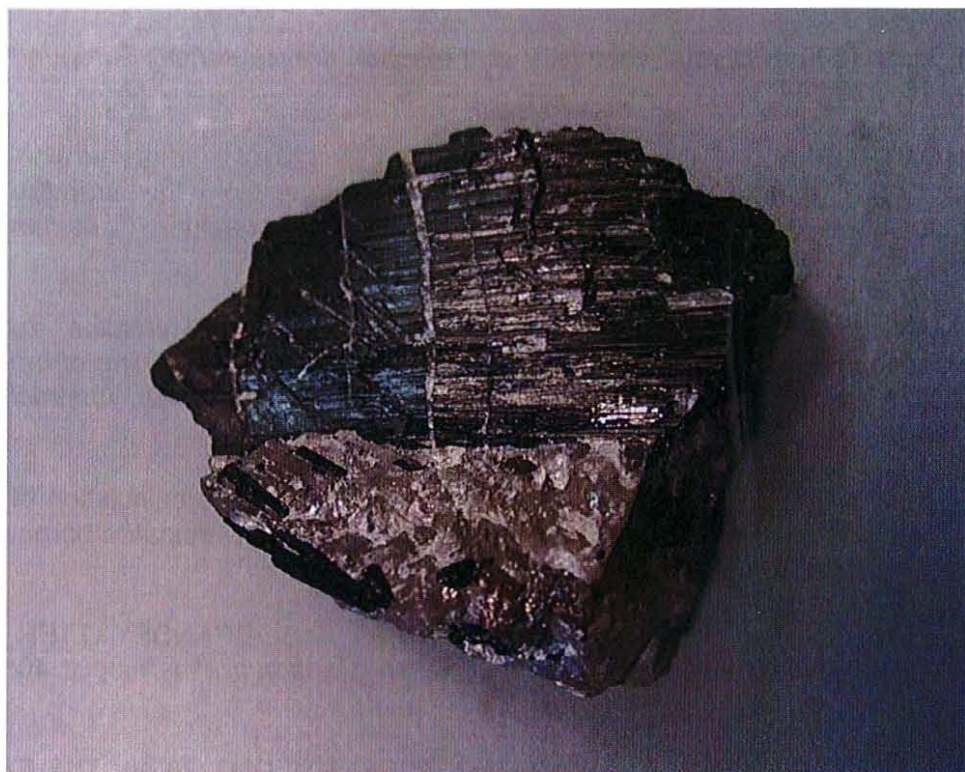


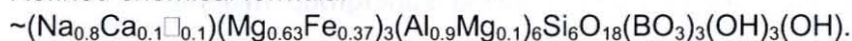
Fig. 5. Ca-, Al- and Mg-rich schorl in pale smokey quartz from Lindvikskollen. Maximum dimension of specimen ca. 3.5 cm. Photo Goran Batic.

Bråstad iron mines, Arendal, Aust-Agder

The sample, showing small (< 2 mm) dark reddish brown translucent prisms, was collected by the first author in 1988. The crystals were originally overgrown by calcite which was removed by dilute HCl. From the structure refinement, it can be concluded that the sample is an essentially F-free dravite containing some Fe and very minor Ca. No SEM-EDS analyses were carried out.

Refined unit-cell parameters: $a = 15.961(2)$, $c = 7.196(1)$ Å.

Refined chemical formula:



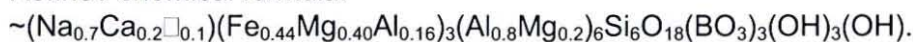
Ramfoss, Snarum, Modum, Buskerud

Ramfoss is a classic locality for black "schorl" crystals occurring in a plagioclase-quartz pegmatite. The sample, a stubby black prism, was collected by the first author in 2009.

According to the structure refinement, it is a Mg-rich, Ca-bearing schorl that contains almost no F. No SEM-EDS analyses were carried out.

Refined unit-cell parameters: $a = 15.995(2)$, $c = 7.224(1)$ Å.

Refined chemical formula:



Acknowledgements

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