

# Savelievaite, $\text{Mg}_2\text{CrO}_2(\text{BO}_3)$ , the first natural borate with species-defining $\text{Cr}^{3+}$ and the ludwigite–savelievaite isomorphous series

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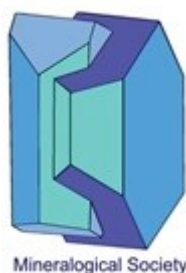
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*Running title:* Savelievaite, a new mineral

## Abstract

A new ludwigite-group mineral savelievaite, ideally  $\text{Mg}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$ , was found in the chromitite body at the Malaya Kharamatalou river valley, Voikar-Syninskiy ultrabasic complex, Polar Urals, Russia. Savelievaite and Cr-enriched ludwigite occur in clinochlore veinlets and are associated with earlier magnesiochromite, spinel, chromite, pargasite, diopside, forsterite, serpentine, magnetite, and pentlandite. Savelievaite forms prismatic, acicular or fibrous crystals up to  $0.05 \times 0.4$  mm usually assembled in radiating or chaotic clusters up to  $1 \times 1.5$  mm across. It is opaque, black to greenish-black. Lustre is vitreous for prismatic crystals and silky for



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fibrous aggregates.  $D(\text{calc.}) = 3.91 \text{ g cm}^{-3}$ . Under the microscope in reflected light, savelievaite is grey, non-pleochroic, with weak bireflectance and anisotropism. The chemical composition (wt.%, EMPA,  $\text{Fe}^{2+}:\text{Fe}^{3+}$  ratio by stoichiometry) is: MgO 34.88, FeO 10.83, NiO 0.36,  $\text{B}_2\text{O}_3$  16.80,  $\text{Al}_2\text{O}_3$  2.97,  $\text{V}_2\text{O}_5$  0.21,  $\text{Cr}_2\text{O}_3$  21.97,  $\text{Fe}_2\text{O}_3$  12.40,  $\text{TiO}_2$  0.43, total 100.85. The empirical formula calculated based on 5 O *apfu* is  $(\text{Mg}_{1.72}\text{Fe}^{2+}_{0.30}\text{Ni}_{0.01})_{\Sigma 2.03}(\text{Cr}^{3+}_{0.57}\text{Fe}^{3+}_{0.31}\text{Al}_{0.12}\text{Ti}_{0.01}\text{V}^{3+}_{0.01})_{\Sigma 1.02}\text{B}_{0.96}\text{O}_5$ . Savelievaite is orthorhombic, space group *Pbam*,  $a = 9.2631(6)$ ,  $b = 12.2298(8)$ ,  $c = 3.0104(2)$  Å,  $V = 341.04(4)$  Å<sup>3</sup>, and  $Z = 4$ . The strongest reflections of the powder XRD pattern [ $d, \text{Å}(l)(hkl)$ ] are: 5.101(100)(120); 2.551(90)(240); 2.524(88)(201); 2.163(36)(250); 2.033(55)(321). The crystal structure was solved from single-crystal X-ray diffraction data and refined to  $R_1 = 0.0405$ . Savelievaite is isostructural with ludwigite,  $\text{Cr}^{3+}$  is concentrated at the *M4* site. The mineral is named in honour of the Russian petrologist and geologist Dr. Galina Nikolaevna Savelieva (b. 1936). Ludwigite, ideally  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ , and savelievaite form a continuous isomorphous series in which  $\text{Cr}^{3+}$  content varies from 0 to 0.60 *apfu*. Occurrences of Cr-enriched (>1 wt.%  $\text{Cr}_2\text{O}_3$ ) varieties of ludwigite are mainly related to ultrabasic complexes. The Cr-richest (>10 wt.%  $\text{Cr}_2\text{O}_3$ ) ludwigite–savelievaite series members are found in chromite ores at Voikar-Syninskiy complex and Volchiegorskoe and Tatischevskoe deposits, both South Urals.

**Keywords:** savelievaite, new mineral, ludwigite, magnesium chromium borate, crystal structure, chromite deposit, Voikar-Syninskiy ultrabasic complex, Urals.

## Introduction

Ludwigite-related minerals form the largest structural family among natural borates. This family (or potential ludwigite supergroup) includes sixteen valid mineral species, which constitute three groups: the ludwigite group, the pinakiolite group, and the orthopinakiolite group. These groups demonstrate some structural differences from each other, however, their structures are related and all sixteen minerals have in fact the same general formula  $M^{2+}_2M^{2++5+}\text{O}_2(\text{BO}_3)$  [for the majority,  $M^{2+}_2M^{3+}\text{O}_2(\text{BO}_3)$ ] in which species-defining cations  $M^{2+} = \text{Mg, Mn, Fe, Ni, Cu}$ ,  $M^{3+} = \text{Al, Cr, Mn, Fe}$ ,  $M^{4+} = \text{Ti}$ , and  $M^{5+} = \text{Sb}$  (Hawthorne *et al.*, 1996; Anthony *et al.*, 2003; The official IMA-CNMNC List..., 2024). Ludwigite, ideally  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ , is a widespread mineral and an important, in places major, boron ore in deposits related to magnesian skarns. Vonsenite, ideally  $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ , is not uncommon (Aleksandrov, 1990; Grew, Anovitz, 1996), but the other minerals related to ludwigite are very rare.

In the present paper, we describe the new ludwigite-group mineral savelievaite, ideally  $\text{Mg}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$ , found in the Voikar-Syninskiy ultrabasic complex in the Polar Urals, Russia. It was named in honour of the Russian petrologist and geologist Dr. Galina Nikolaevna Savelieva (born 1936) who worked at the Geological Institute of the Russian Academy of Sciences, Moscow. She made a great contribution to the petrology and geology of ophiolites and, in particular, studied the Voikar-Syninskiy complex in detail. Both the mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2021–051) (Pekov *et al.*, 2021). The type specimen of savelievaite is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 97680.

Savelievaite is the first borate mineral with species-defining  $\text{Cr}^{3+}$ . Before its discovery, only one mineral with both species-defining boron and chromium was known, iquiqueite  $\text{K}_3\text{Na}_4\text{Mg}(\text{Cr}^{6+}\text{O}_4)\text{B}_{24}\text{O}_{39}(\text{OH})\cdot 12\text{H}_2\text{O}$ , found in nitratine deposits in Chile (Ericksen *et al.*, 1986). Unlike savelievaite, iquiqueite is a supergene hydrous chromate-borate with  $\text{Cr}^{6+}$ . All other minerals with both species-defining Cr are B are borosilicates of the tourmaline group.

As our and earlier published data show, ludwigite and savelievaite form a continuous isomorphous series. The chemical variation of its members is also a subject of this paper.

## Occurrence

The specimen which became the holotype of savelievaite was found in 2005 by one of the authors (N.V.V.) on the left bank of the Malaya Kharamatalou river valley, northern part of the Voikar-Syninskiy (another spelling: Voykar-Synya) ultrabasic complex, Shuryshkarskiy District, Yamalo-Nenets Autonomous Okrug, Polar Urals (66°39'57"N, 64°41'50.1"E). The geology of this area is described by Savelieva *et al.* (2015).

The specimen was collected from the chromitite body localized within olivine-antigorite rocks (so-called voikarites) formed as a result of the metasomatic alteration of rocks belonging to a dunite-harzburgite complex. The chromitite mainly consists of members of the magnesiochromite – chromite – (Cr,Fe)-rich spinel solid-solution system. Savelievaite and Cr-enriched variety of ludwigite occur in clinochlore veinlets cross-cutting massive, coarse-grained chromitite (Fig. 1). These borates are associated with greenish Cr-bearing (1.5–2.5 wt.%  $\text{Cr}_2\text{O}_3$ ) clinochlore and earlier magnesiochromite, spinel (Cr- and Fe-rich variety), chromite, pargasite (Cr-bearing variety), diopside (Cr- and Al-bearing variety), forsterite, serpentine, magnetite, and pentlandite.

Also we studied Cr-enriched ludwigite from the Tatishchevskoe chromite deposit located near the Novyi Mir town, Varna District, Chelyabinsk Oblast, South Urals, Russia. It occurs in veinlets consisting of pale lilac Cr-bearing clinocllore which crosscut massive chromitite.

### **General Appearance, Physical Properties and Optical Data**

Savelievaite forms prismatic to acicular or fibrous crystals, in places with rhomb-like cross-section, up to 0.4 mm long and up to 0.05 mm thick. Savelievaite crystals are elongated along [001], their prismatic zone is formed by the  $\{hk0\}$  faces and the terminations are very crude. Some crystals are curved, divergent, and typically assembled in radiating (spray- or sheaf-like) or chaotic clusters (Fig. 1). Aggregates of savelievaite, intimately intergrown with clinocllore, are up to  $1 \times 1.5$  mm across. A Cr-enriched variety of ludwigite visually indistinguishable from savelievaite forms here similar aggregates up to 2 mm across.

Prismatic and acicular crystals of savelievaite are opaque and black in color, whereas the thinnest fibrous individuals are translucent and greenish black. The streak is greyish-green. The lustre is strong vitreous for prismatic crystals and silky for fibrous aggregates. The mineral is brittle. Cleavage or parting was not observed, the fracture is uneven. The Mohs hardness is *ca.* 5. Density calculated using the empirical formula and unit-cell volume obtained from single-crystal X-ray diffraction (XRD) data is  $3.91 \text{ g cm}^{-3}$ . The mineral is very weakly ferromagnetic.

Under the microscope in reflected light, savelievaite is grey, pleochroism was not observed. Bireflectance and anisotropism are weak. Internal reflections were not observed. The reflectance values measured in air by means of the MSF-21 microspectrophotometer (LOMO, Russia) using the No. 545 Zeiss SiC standard are reported in Table 1.

Chromium-bearing ludwigite at the Tatishchevskoe deposit occurs as opaque black long-prismatic to acicular crystals up to 1.5 cm long. They are typically split to form sheafs. The crystals and their clusters are embedded in fine-grained clinocllore aggregates.

### **Raman Spectroscopy**

The Raman spectrum of savelievaite (Fig. 2, curve a) was obtained for an aggregate of randomly oriented crystals using an EnSpectr R532 spectrometer (Dept. of Mineralogy, Moscow State University, Russia) with a green laser (532 nm) at room temperature. The spectrometer is equipped with a CCD detector. The calibration of the device was carried out along a  $520 \text{ cm}^{-1}$  crystalline silicon line. The output power of the laser beam was 7 mW. The diameter of the focal spot on the sample was about 10  $\mu\text{m}$ . The backscattered Raman signal was collected with  $40\times$  objective. Signal acquisition time for a single scan was 3 s and the signal was averaged over 150 scans. The spectrum was processed using the EnSpectr expert mode program in the range from

200 to 4000  $\text{cm}^{-1}$  with the use of a holographic diffraction grating with 1800 lines per millimeter and a resolution of 6  $\text{cm}^{-1}$ .

For comparison, the Raman spectra of common<sup>1</sup> black ludwigite from the Akhmatovskaya Pit (South Urals, Russia) (Fig. 2, curve b) and dark green ludwigite from Gavasai (Kuraminsky Range, Uzbekistan), chemically close to the end-member  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$  (Fig. 2, curve c), were obtained under the same conditions.

The Raman spectrum of savelievaite is in whole similar to the spectra of ludwigite. According to data reported by Leite *et al.* (2002), Nakamoto (2006), Enholm (2016), and Bilohuščin *et al.* (2017), there are several groups of bands in the Raman spectra of ludwigite-group borates. The very weak and broad band between 1100 and 1400  $\text{cm}^{-1}$  corresponds to B–O antisymmetric stretching vibrations ( $\nu_3$ ) of triangular  $(\text{BO}_3)^{3-}$  groups. The bands in the range 520–700  $\text{cm}^{-1}$  belong to the  $\nu_4$  antisymmetric bending vibrations of B–O bonds. The series of bands between 300 and 500  $\text{cm}^{-1}$  can be assigned to M–O stretching and bending modes. Bands with Raman shift lower than 300  $\text{cm}^{-1}$  are interpreted as lattice modes.

Band of B–O symmetric stretching vibrations ( $\nu_1$ ) was not observed either in the Raman spectrum of savelievaite or in the spectrum of ludwigite from the Akhmatovskaya Pit), in contrast to the spectrum of the chemically close to the end-member  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$  ludwigite from Gavasai, in which this distinct narrow band is located near 950  $\text{cm}^{-1}$ . The absence of the  $\nu_1$  modes in Raman spectra of common ludwigite  $(\text{Mg},\text{Fe}^{2+})_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$  and vonsenite  $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$  was also reported by Leite *et al.* (2002) and Bilohuščin *et al.* (2017). In Fig. 3 the Raman spectra of two chemically different varieties of ludwigite published by Bilohuščin *et al.* (2017) are shown. The band of symmetric stretching vibrations ( $\nu_1$ : 959  $\text{cm}^{-1}$ ) occurs only in the spectrum of the Mg- and Al-enriched and  $\text{Fe}^{2+}$ -depleted variety. The band corresponding to the  $\nu_3$  mode, which is characterized by being broad and of low intensity, is observed in all the Raman spectra presented in Figs. 2 and 3.

## Chemical Data

Chemical data for minerals of the ludwigite–savelievaite series from the Voikar-Syninskiy complex were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 10 nA; the electron beam was rastered on a  $3 \times 3 \mu\text{m}^2$  area. The following standards were used: MgO (Mg), Fe (Fe), Ni (Ni), LaB<sub>6</sub> (B), Al<sub>2</sub>O<sub>3</sub> (Al), V (V),

<sup>1</sup> The term "common ludwigite" means, here and below, ludwigite with the chemical composition in the range the most typical for magnesian skarns (see Aleksandrov, 1990; Aleksandrov and Troneva, 2000, 2004).

Cr (Cr), and Ti (Ti). The content of other elements with an atomic number >6, except oxygen, are below detection limits.

The chemical composition of Cr-bearing ludwigite from the Tatishchevskoe deposit was determined using a Hitachi FlexSEM 1000 scanning electron microscope equipped with EDS Xplore Contact 30 detector and Oxford AZtecLive STD system of analysis. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current, and a beam diameter of 1  $\mu\text{m}$ . The following standards were used:  $\text{Mg}_2\text{SiO}_4$  (Mg),  $\text{FeS}_2$  (Fe), Ni (Ni), Cr (Cr) and Ti (Ti).

Representative analyses of the studied minerals are given in Table 2. The empirical formula of the holotype savelievaite calculated on the basis of 5 O atoms per formula unit (*apfu*) is  $(\text{Mg}_{1.72}\text{Fe}^{2+}_{0.30}\text{Ni}_{0.01})_{\Sigma 2.03}(\text{Cr}^{3+}_{0.57}\text{Fe}^{3+}_{0.31}\text{Al}_{0.12}\text{Ti}_{0.01}\text{V}^{3+}_{0.01})_{\Sigma 1.02}\text{B}_{0.96}\text{O}_5$  (the  $\text{Fe}^{2+}:\text{Fe}^{3+}$  ratio was calculated by stoichiometry). The simplified formula of the new mineral is  $(\text{Mg},\text{Fe}^{2+})_2(\text{Cr}^{3+},\text{Fe}^{3+},\text{Al})\text{BO}_5$  and the ideal, end-member formula is  $\text{Mg}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$  which requires MgO 42.11,  $\text{B}_2\text{O}_3$  18.19,  $\text{Cr}_2\text{O}_3$  39.70, total 100 wt%.

### X-ray Crystallography and Crystal Structure Determination

Powder XRD studies of savelievaite were performed on a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry,  $\text{CoK}\alpha$  radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA and an exposure time of 15 min. Angular resolution of the detector is  $0.045\ 2\theta$  (pixel size 0.1 mm). The data were integrated using the software package Osc2Tab (Britvin *et al.*, 2017). Powder XRD data of savelievaite are given in Table 3. The orthorhombic unit cell parameters refined from the powder data are:  $a = 9.263(2)$ ,  $b = 12.229(2)$ ,  $c = 3.012(1)$  Å, and  $V = 341.1(2)$  Å<sup>3</sup>.

A single-crystal XRD study of savelievaite was carried out using an Xcalibur S diffractometer equipped with a CCD detector ( $\text{MoK}\alpha$  radiation). More than a hemisphere of three-dimensional data was collected. Data reduction was performed using CrysAlisPro version 1.171.39.46 (Rigaku..., 2018). The data were corrected for Lorentz factor and polarization effect. The crystal structure was solved by direct methods and refined using the SHELX software package (Sheldrick, 2015) to  $R = 0.0405$  on the basis of 410 independent reflections with  $I > 2\sigma(I)$ . The occupancies of the *M*1-3 sites were refined as Mg vs Fe, for the *M*4 site Cr vs Al was used. Crystal data, data collection information and structure refinement details are given in Table 4, coordinates and equivalent displacement parameters of atoms in Table 5, and selected interatomic distances in Table 6.

A single-crystal XRD study of Cr-enriched ludwigite from Tatishchevskoe was carried out using the same diffractometer. The obtained orthorhombic unit cell parameters are:  $a = 9.272(7)$ ,  $b = 12.30(3)$ ,  $c = 3.028(3)$  Å, and  $V = 345.2(9)$  Å<sup>3</sup>.

## Discussion

### *Crystal structure and comparative crystal chemistry*

Savelievaite is a representative of the well-known ludwigite structure type (Takéuchi *et al.*, 1950; Bertaut, 1950). Its crystal structure (Fig. 4) is built by the walls of edge-sharing octahedra  $M1-4$  centred by metal cations  $M$ . According to Hawthorne *et al.* (1996), ludwigite-type compounds belong to so-called “3 Å wallpaper structures”. They consist of chains of edge-sharing octahedra cross-linked by  $\text{BO}_3$  triangles. In ludwigite structure type the chains are connected with each other forming dense zig-zag sheets (walls) with five octahedra on the zig and three octahedra on the zag. Adjacent sheets are connected *via* common oxygen vertices of octahedra forming triangular tunnels in which  $\text{BO}_3$  triangles sharing O vertices with the octahedra are located. There are four crystallographically independent  $M$  sites in the ludwigite-type structure. In savelievaite, trivalent cations are located in the smallest  $M4$  octahedron with average  $M4 - \text{O}$  distance of 2.027 Å (Table 6), as well as in other ludwigite-group minerals and related synthetic compounds in which the majority or  $M^{3+}$  cations are located at the same site (Norrestam *et al.*, 1989; Takéuchi and Kogure, 1992; Irwin and Peterson, 1999; Appel and Brigatti, 1999; Holtstam, 2001; Brovkin *et al.*, 2002). The refined number of electrons ( $e_{\text{ref}}$ ) in the  $M4$  site in savelievaite is 21.91 which is in agreement with the Cr prevailing in this site. The refinement of site occupancies for the  $M1$ ,  $M2$  and  $M3$  sites showed that  $M1$  and  $M2$  are strongly Mg-dominant (96-97% Mg) with only minor Fe, whereas the  $M3$  site hosts much more Fe: the Mg:Fe ratio is 0.64:0.36 (Table 5). The average  $M1-M3 - \text{O}$  distances are 2.08 – 2.09 Å which also confirms the occurrence of Mg at the  $M1-3$  sites (Table 6). Such cation distribution between the  $M$  sites in savelievaite is in a good agreement with previously published data on other ludwigite-group minerals (see references above).

Thus, savelievaite, ideally  $\text{Mg}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$ , is a member of the ludwigite group, the  $\text{Cr}^{3+}$  analogue of ludwigite  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$  and fredrikssonite  $\text{Mg}_2\text{Mn}^{3+}\text{O}_2(\text{BO}_3)$  with Cr the dominant trivalent cation occupying the  $M4$  site (Tables 5 and 7).

A compound isostructural with ludwigite,  $\text{Ni}^{2+}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$  [orthorhombic,  $Pbam$ ,  $a = 9.209(1)$ ,  $b = 12.121(1)$ ,  $c = 2.9877(3)$  Å, and  $V = 333.49(6)$  Å<sup>3</sup>] has been synthesized (Norrestam *et al.*, 1994). In this borate the  $M2$  and  $M3$  sites contain only 6 and 11 at.% Cr, respectively, while the  $M4$  site, like savelievaite, is Cr-dominant: 88% Cr and 12% Ni (the numbering of  $M$  sites corresponds to savelievaite).

### *Ludwigite–savelievaite isomorphous series*

Minor chromium substitution (up to 0.2 wt.% Cr<sub>2</sub>O<sub>3</sub>) is not very rare in ludwigite (Aleksandrov and Troneva, 1998, 2000), whereas varieties of this mineral containing as much as several wt.% Cr<sub>2</sub>O<sub>3</sub> have been described from only few localities. A ludwigite variety containing up to 4.0 wt.% Cr<sub>2</sub>O<sub>3</sub> was first reported in specimens of a carbonate-forsterite rock with magnesiochromite and sulfides found in dumps of the Hayama nickel mine, Date District, Fukushima Prefecture, Japan (Kato *et al.*, 1988). S.M. Aleksandrov and M.A. Troneva, who systematically studied the chemical variation of ludwigite-related borates, published original electron microprobe analyses of Cr-enriched ludwigite from the Hayama mine (up to 2.9 wt.% Cr<sub>2</sub>O<sub>3</sub>), from altered dunite of the Jumbo Mountain nickel deposit, Snohomish Co., Washington, USA (up to 5.7 wt.% Cr<sub>2</sub>O<sub>3</sub>: Aleksandrov and Troneva, 1998, 2000), from calciphyre of the Nikolae-Maksimilianovskaya Pit, Zlatoust District, South Urals, Russia (6.5 wt.% Cr<sub>2</sub>O<sub>3</sub>: Aleksandrov and Troneva, 2004), and from the Tatishchevskoe deposit (up to 10.4 wt.% Cr<sub>2</sub>O<sub>3</sub>, without sample description: Aleksandrov and Troneva, 2008). The highest chromium content in ludwigite (and in a natural borate in general) was reported, before our work, for samples from chromite ores of the Volchiegorskoe chromium deposit, Verkhniy Ufaley District, South Urals, Russia: up to 17.25 wt.% Cr<sub>2</sub>O<sub>3</sub> that corresponds to 0.45 *apfu* Cr<sup>3+</sup> (Tolkanov *et al.*, 2000). Chromium-bearing ludwigite was also mentioned from chromite deposits related to the Khadatinsky basite-ultrabasic massif at Polar Urals and the Verblyuzhiegorsky ultrabasic massif at South Urals, both Russia. In ludwigite from these localities, up to 5–7 wt.% Cr<sub>2</sub>O<sub>3</sub> was detected (Kuznetsov, 2003), however, other chemical data for these samples were not reported.

In chromite ores of the Voikar-Syninskiy complex, ludwigite was first found by Mel'nitsky (1958) and later briefly described, in the samples collected by G.N. Savelieva, by Graudin' and Baklanov (1973). However, its chemical composition was not studied. Aleksandrov and Troneva (1998), taking into account the earlier reported data on mineral association and optical properties of the Voikar-Syninskiy ludwigite, suggested that it can be Cr-rich. Our data confirmed this suggestion.

Representative selection of earlier published analyses of Cr-enriched ludwigite is given, together with our analyses, in **Table 2**. All analyses of ludwigite with > 1 wt.% Cr<sub>2</sub>O<sub>3</sub> are plotted in a diagram showing the relative proportions of trivalent cations and Ti in ludwigite and savelievaite (**Fig. 5**). Thus, ludwigite and savelievaite form a continuous solid-solution series in which the Cr<sup>3+</sup> content ranges from 0 to 0.60 *apfu*, corresponding to 0–23 wt.% Cr<sub>2</sub>O<sub>3</sub>. The main variable value in this series is the Fe<sup>3+</sup>:Cr ratio, Al plays subordinate but perceptible role whereas other *M*<sup>3+,4+</sup> cations (V, Ti) seem insignificant. All the samples plotted in **Fig. 5** had been studied using XRD and/or optical methods (Kato *et al.*, 1988; Aleksandrov and Troneva, 1998, 2000,



2004, 2008; Tolkanov *et al.*, 2000; our data), which confirm that the analyzed minerals belonged to the ludwigite group and that these solid solutions constitute a true isomorphous series. The synthesis of  $\text{Ni}^{2+}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$ , a compound with only Cr as trivalent *M* cation, isostructural to ludwigite (Norrestam *et al.*, 1994) implies that savelievaite or its Ni-dominant analogue with Cr > 0.60 *apfu* could occur naturally.

Chromium-enriched borate minerals are rare primarily due to quite different geochemistry of Cr and B: chromium-rich and boron-rich types of mineralization form in separate geological settings. However, in some cases the "geochemical ways" of these chemical elements cross that result in formation of minerals enriched in both Cr and B. If a such mineral-forming system is Si-rich then Cr-bearing tourmalines appear (Rumyantseva, 1983; Reznitskii *et al.*, 2014) whereas in Si-depleted environments Cr-enriched borates can crystallize. Except for the Nikolae-Maksimilianovskaya Pit at South Urals where Cr-bearing ludwigite was found in a calciphyre zone of magnesian skarn formed at the contact between gabbro and dolomites, all known localities of Cr-enriched (> 1 wt.%  $\text{Cr}_2\text{O}_3$ ) ludwigite-group minerals are chromite or nickel deposits related to ultrabasic massifs, and thus we do not doubt that ultrabasic rocks are the source of chromium for these borates. Moreover, we note that at three Uralian localities where the Cr-richest members of the described series were found, namely the Voikar-Syninskiy complex, Volchiegorskoe and Tatischevskoe chromium deposits, the borate mineralization occurs in hydrothermal assemblages directly within chromite orebodies. We do not think that ultrabasic rocks were a source of boron and we believe that in all these cases neighbouring bodies of more acidic rock provided boron. In the Voikar-Syninskiy complex, besides ultrabasic rocks, only gabbroid dykes occur near the savelievaite locality, and we cannot suggest a geochemically substantiated source of boron.

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Table 1. Reflectance data ( $R$ , %) of savelievaite.

$\lambda$ (nm)	$R_{\max}$	$R_{\min}$	$\lambda$ (nm)	$R_{\max}$	$R_{\min}$
400	11.5	9.9	560	10.4	8.6
420	11.5	9.9	580	10.4	8.5
440	11.4	9.7	<b>589</b>	<b>10.3</b>	<b>8.4</b>
460	11.2	9.4	600	10.3	8.4
<b>470</b>	<b>11.1</b>	<b>9.2</b>	620	10.2	8.1
480	11.0	9.1	640	10.1	7.9
500	10.8	9.0	<b>650</b>	<b>10.0</b>	<b>7.9</b>
520	10.6	8.8	660	10.0	7.8
540	10.5	8.7	680	9.8	7.7
<b>546</b>	<b>10.5</b>	<b>8.7</b>	700	9.8	7.5

Data for wavelengths recommended by the IMA Commission on ore microscopy (COM) are marked in boldtype.

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Table 2. Chemical composition of savelievaite (1–8) and Cr-enriched ludwigite (9–22).

	1	2	3	4	5	6	7	8	9	10	11	12
	wt. %											
MgO	34.88 [34.08 – 35.72]	34.52	34.30	34.11	34.83	33.87	33.88	32.97	32.18	32.15	31.96	32.77
FeO	10.83	10.99	10.49	11.37	10.94	11.16	11.54	12.10	13.76	13.12	12.11	11.10
NiO	0.36 [0.32 – 0.43]	0.35	0.37	0.33	0.41	0.37	0.36	0.38	0.33	0.33	0.68	0.50
B <sub>2</sub> O <sub>3</sub>	16.80 [15.97 – 17.96]	17.03	16.79	17.15	16.96	17.60	17.01	16.94	17.13	16.61	(17.0)	(16.9)
Al <sub>2</sub> O <sub>3</sub>	2.97 [2.54 – 3.38]	2.50	2.75	2.99	3.70	3.08	3.09	2.79	2.96	2.98	-	-
V <sub>2</sub> O <sub>3</sub>	0.21 [0.17 – 0.24]	0.19	0.23	0.18	0.27	0.22	0.27	0.27	0.25	0.29	-	-
Cr <sub>2</sub> O <sub>3</sub>	21.97 [21.28 – 22.99]	22.78	21.83	20.62	20.26	19.46	17.91	16.55	12.37	11.44	11.25	8.22
Fe <sub>2</sub> O <sub>3</sub>	12.40	12.21	12.13	13.67	13.17	13.98	15.05	16.41	21.10	20.98	26.99	29.75
TiO <sub>2</sub>	0.43 [0.26 – 0.69]	0.29	0.67	0.26	0.43	0.53	0.99	0.84	0.90	1.40	0.21	0.28
Total	100.85	100.86	99.56	100.68	100.97	100.27	100.10	99.25	100.98	99.30	100.20	99.52
	formula calculated based on 5 O atoms per formula unit ( <i>apfu</i> )											
Mg	1.72	1.71	1.71	1.69	1.71	1.67	1.68	1.66	1.60	1.63	1.63	1.67
Fe <sup>2+</sup>	0.30	0.30	0.29	0.32	0.30	0.31	0.32	0.34	0.38	0.37	0.35	0.32
Ni	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
ΣM <sup>2+</sup>	2.03	2.02	2.01	2.02	2.02	1.99	2.01	2.01	1.99	2.01	2	2
Al	0.12	0.10	0.11	0.12	0.14	0.12	0.12	0.11	0.12	0.12	-	-
V	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	-	-
Cr	0.57	0.60	0.58	0.54	0.53	0.51	0.47	0.44	0.33	0.31	0.30	0.22
Fe <sup>3+</sup>	0.31	0.30	0.31	0.34	0.33	0.35	0.38	0.42	0.53	0.54	0.69	0.77
Ti	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.04	0.01	0.01
ΣM <sup>3+,4+</sup>	1.02	1.02	1.03	1.01	1.02	1.00	1.00	1.00	1.01	1.02	1	1
B	0.96	0.97	0.97	0.98	0.96	1.01	0.98	0.99	0.99	0.97	1	1

Table 2 (continues).

	13	14	15	16	17	18	19	20	21	22
wt.%										
MgO	33.08	35.42	36.81	36.07	35.62	26.54	30.51	37.19	37.81	40.41
MnO	-	-	-	-	-	0.01	0.07	-	-	0.07
FeO	11.31	7.85	6.82	7.91	9.01	19.77	16.27	6.54	5.47	3.51
NiO	0.78	0.85	0.51	0.52	0.52	0.09	-	-	-	0.02
B <sub>2</sub> O <sub>3</sub>	(17.2)	(17.4)	(17.7)	(17.5)	(17.6)	(16.3)	(17.1)	(17.6)	(17.7)	(18.3)
Al <sub>2</sub> O <sub>3</sub>	0.10	0.10	1.62	1.48	1.46	0.30	4.08	2.46	2.55	2.52
V <sub>2</sub> O <sub>3</sub>	-	-	0.20	0.17	0.24	0.10	0.09	-	-	-
Cr <sub>2</sub> O <sub>3</sub>	4.73	10.37	17.25	13.45	9.26	6.50	5.68	1.09	4.02	2.78
Fe <sub>2</sub> O <sub>3</sub>	33.79	28.57	19.20	23.40	27.50	29.80	27.11	35.12	32.45	35.16
TiO <sub>2</sub>	0.41	0.24	0.29	0.26	0.57	0.26	0.07	-	-	0.11
Total	101.40	100.80	100.40	100.76	101.78	99.67*	100.98*	100**	100**	102.88*
formula calculated based on 5 O atoms per formula unit ( <i>apfu</i> )										
Mg	1.66	1.76	1.80	1.77	1.74	1.41	1.54	1.83	1.85	1.91
Fe <sup>2+</sup>	0.32	0.22	0.19	0.22	0.25	0.59	0.46	0.17	0.15	0.09
Ni	0.02	0.02	0.01	0.01	0.01	0.00	-	-	-	-
ΣM <sup>2+</sup>	2	2	2	2	2	2	2	2	2	2
Al	0.00	0.00	0.06	0.06	0.06	0.01	0.16	0.10	0.10	0.09
V	-	-	0.01	0.00	0.01	0.00	0.00	-	-	-
Cr	0.13	0.27	0.45	0.35	0.24	0.18	0.15	0.03	0.10	0.07
Fe <sup>3+</sup>	0.86	0.72	0.47	0.58	0.68	0.80	0.69	0.87	0.80	0.84
Ti	0.01	0.01	0.01	0.01	0.01	0.01	0.00	-	-	0.00
ΣM <sup>3+,4+</sup>	1	1	1	1	1	1	1	1	1	1
B	1	1	1	1	1	1	1	1	1	1

1–10 – Voikar-Syninskiy complex (our data; 1 – savelievaite holotype, averaged for 12 spot analyses, ranges are in brackets); 11–14 – Tatishchevskoe deposit (11–12: our data, 13–14: Aleksandrov and Troneva, 2008); 15–17 – Volchiegorskoe deposit (Tolkanov *et al.*, 2000); 18 – Nikolae-Maksimilianovskaya Pit (Aleksandrov and Troneva, 2004); 19 – Jumbo Mountain deposit (Aleksandrov and Troneva, 1998); 20–22 – Hayama mine (20–21: Kato *et al.*, 1988, 22: Aleksandrov and Troneva, 1998). In analyses 1–10 contents of FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated by charge balance. In analyses 11–22 boron content was not measured but calculated by stoichiometry, for 1 B *apfu* (calculated B<sub>2</sub>O<sub>3</sub> content is given in parentheses), and the Fe<sup>2+</sup>:Fe<sup>3+</sup> ratio was calculated by charge balance for the formula (M<sup>2+</sup>)<sub>2</sub>(M<sup>3+,4+</sup>)<sub>1</sub>B<sub>1</sub>O<sub>5</sub>; the literature analyses 11–19 and 22 were re-calculated by us

in accordance with this scheme. \*Minor amounts of Ca, Co, Si, Sn and/or Sb are not included. \*\*Total was recalculated for 100% by Kato *et al.* (1988). Dash means the content below the detection limit or a constituent was not determined.

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Table 3. Powder X-ray diffraction data ( $d$  in Å) of savelievaite.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
8	7.37	7	7.384	110	7	1.773	8	1.773	520
9	6.11	7	6.115	020			3	1.762	341
<b>100</b>	<b>5.101</b>	100	5.103	120	12	1.758	13	1.758	421
5	3.729	3	3.731	130			2	1.757	251
4	3.057	3	3.057	040	5	1.717	3	1.717	170
<b>24</b>	<b>3.008</b>	24	3.010	001	3	1.701	3	1.701	360
		10	2.994	310	7	1.661	10	1.660	161
8	2.904	6	2.903	140	7	1.585	6	1.586	261
10	2.788	10	2.788	111	<b>25</b>	<b>1.574</b>	35	1.574	441
10	2.756	13	2.756	320			9	1.529	080
7	2.701	7	2.701	021	20	1.529	20	1.528	521
<b>90</b>	<b>2.551</b>	98	2.552	240			3	1.508	180
<b>88</b>	<b>2.524</b>	100	2.524	201	22	1.506	32	1.505	002
13	2.336	8	2.343	131	<b>23</b>	<b>1.492</b>	33	1.491	171
		11	2.333	221			8	1.481	361
5	2.318	7	2.316	400	8	1.479	4	1.477	550
2	2.274	1	2.275	410	17	1.472	23	1.471	531
<b>36</b>	<b>2.163</b>	35	2.163	250	3	1.445	5	1.444	122
17	2.147	7	2.146	231	2	1.403	2	1.402	541
		12	2.145	041			23	1.378	640
<b>24</b>	<b>2.123</b>	29	2.123	311	14	1.378	3	1.374	601
<b>55</b>	<b>2.033</b>	67	2.033	321	3	1.364	5	1.363	081
15	1.992	14	1.991	160			4	1.349	181
6	1.947	9	1.946	241	3	1.348	1	1.345	312
<b>29</b>	<b>1.906</b>	36	1.906	331	3	1.321	3	1.321	322
6	1.866	7	1.866	260			5	1.308	281
2	1.845	1	1.846	440	4	1.307	2	1.306	650
3	1.834	2	1.836	401					
		1	1.832	510					

\*For the calculated pattern, only reflections with intensities  $\geq 1$  are given; \*\*for the unit-cell parameters obtained from single-crystal data. The strongest reflections are marked in boldtype.

Table 4. Crystal data, data collection information and structure refinement details for savelievaite.

Crystal system, space group, $Z$	Orthorhombic, $Pbam$ , 4
Unit-cell dimensions, Å	$a = 9.2631(6)$ $b = 12.2298(8)$ $c = 3.0104(2)$
$V$ , Å <sup>3</sup>	341.04(4)
Crystal size, mm <sup>3</sup>	0.02 × 0.03 × 0.06
Diffractometer	Xcalibur S CCD
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073
Temperature, K	293(2)
Absorption correction	multi-scan
$\theta$ range for data collection, °	2.758 – 28.249
Index ranges	$-12 \leq h \leq 10$ , $-16 \leq k \leq 15$ , $-4 \leq l \leq 3$
Reflections collected	2427
Independent reflections	496 ( $R_{\text{int}} = 0.0731$ )
Independent reflections with $I > 2\sigma(I)$	410
Refinement method	full-matrix least-squares on $F^2$
Number of refined parameters	62
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0405$ , $wR2^* = 0.0427$
$R$ indices (all data)	$R1 = 0.0589$ , $wR2^* = 0.0459$
GoF	0.990
Largest diff. peak and hole, e/Å <sup>3</sup>	0.50 [1.50 Å from O4] and -0.57 [1.71 Å from O3]

\*  $w = 1/[\sigma^2(F_o^2) + (0.0055P)^2]$ ;  $P = \{[\max(0, F_o^2)] + 2F_c^2\}/3$

Table 5. Coordinates and equivalent displacement parameters ( $U_{eq}$ , in  $\text{\AA}^2$ ) of atoms and site occupancy factors (s.o.f.) for savelievaite.

Site	$x$	$y$	$z$	$U_{eq}$	s.o.f.
<i>M1</i>	0.0	0.0	0.5	0.0052(7)	Mg <sub>0.959(6)</sub> Fe <sub>0.041(6)</sub>
<i>M2</i>	0.00053(17)	0.27911(12)	0.5	0.0050(5)	Mg <sub>0.973(5)</sub> Fe <sub>0.027(5)</sub>
<i>M3</i>	0.5	0.0	0.0	0.0072(5)	Mg <sub>0.644(7)</sub> Fe <sub>0.356(7)</sub>
<i>M4</i>	0.24039(9)	0.11370(6)	0.0	0.0033(3)	"Cr <sub>0.810(11)</sub> Al <sub>0.190(11)</sub> "*
B	0.2715(6)	0.3605(5)	0.0	0.0103(12)	B <sub>1.00</sub>
O1	0.3480(3)	0.4572(3)	0.0	0.0102(8)	O <sub>1.00</sub>
O2	0.1103(3)	0.1428(3)	0.5	0.0109(8)	O <sub>1.00</sub>
O3	0.1228(3)	0.3580(3)	0.0	0.0114(8)	O <sub>1.00</sub>
O4	0.3823(3)	0.0768(3)	0.5	0.0122(9)	O <sub>1.00</sub>
O5	0.3465(4)	0.2622(3)	0.0	0.0102(9)	O <sub>1.00</sub>

\*The occupancy of the mixed-occupied *M4* site was refined as Cr vs Al; in the result, the formal Cr:Al ratio of 0.81:0.19 was obtained that corresponds to refined number of electrons  $e_{ref} = 21.91$ .

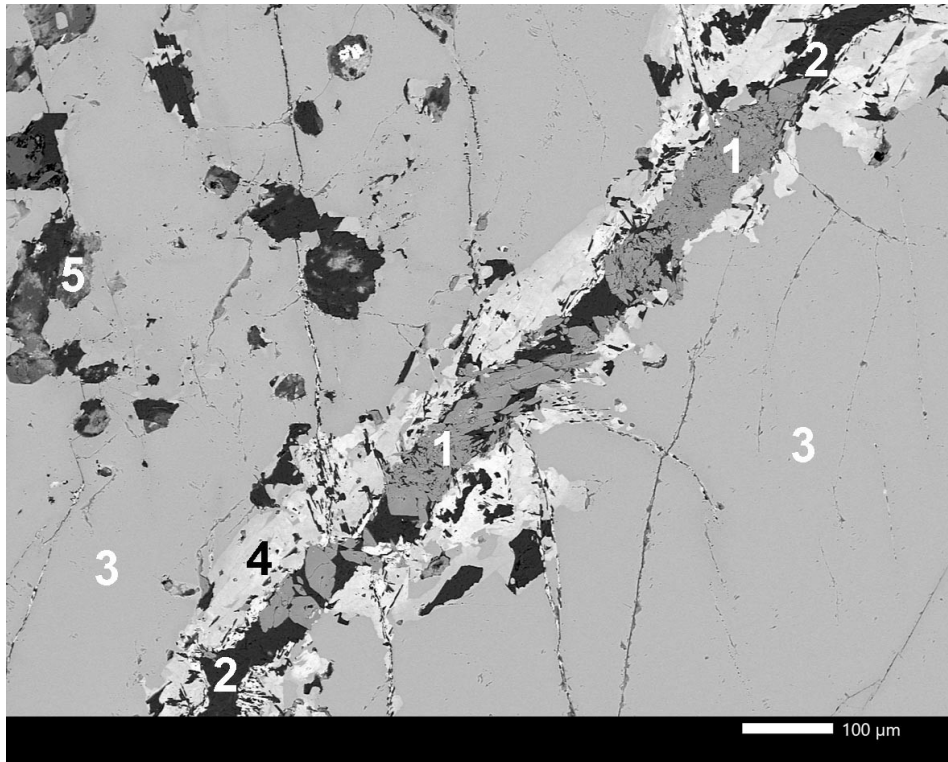
Table 6. Selected interatomic distances ( $\text{\AA}$ ) in the structure of savelievaite.

<i>M1</i> - O2 2.023(3) x 2	<i>M3</i> - O3 2.076(3) x 2	B - O3 1.378(6)
- O1 2.127(2) x 4	- O4 2.082(2) x 4	- O1 1.379(6)
< <i>M1</i> -O> 2.092	< <i>M3</i> -O> 2.080	- O5 1.389(6)
		<B - O> 1.382
<i>M2</i> - O2 1.953(4)	<i>M4</i> - O2 1.960(2) x 2	
- O4 2.075(4)	- O4 2.049(2) x 2	
- O3 2.117(3) x 2	- O5 2.065(3)	
- O5 2.134(3) x 2	- O1 2.081(3)	
< <i>M2</i> -O> 2.088	< <i>M4</i> -O> 2.027	

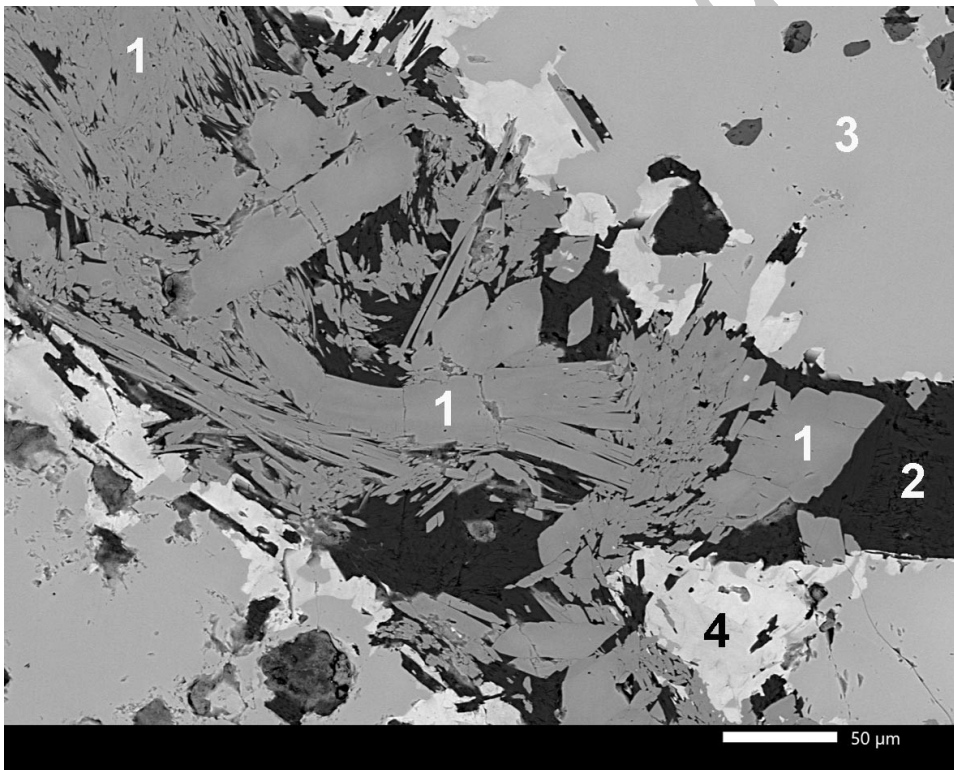
Table 7. Comparative characteristics of savelievaite, ludwigite and fredrikssonite.

Mineral	Savelievaite	Ludwigite	Fredrikssonite
Ideal formula	$\text{Mg}_2\text{Cr}^{3+}\text{O}_2(\text{BO}_3)$	$\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$	$\text{Mg}_2\text{Mn}^{3+}\text{O}_2(\text{BO}_3)$
Crystal system	Orthorhombic		
Space group	<i>Pbam</i>		
<i>Unit cell data:</i>			
<i>a</i> , Å	9.2631 (6)	9.241	9.198
<i>b</i> , Å	12.2298 (8)	12.295	12.528
<i>c</i> , Å	3.0104 (2)	3.021	2.965
<i>V</i> , Å <sup>3</sup>	341.04 (2)	343	341.7
<i>Z</i>	4	4	4
Strong lines of	5.101 (100)	5.12 (100)	5.16 (80)
the powder	3.008 (24)	2.990 (25)	2.590 (100)
X-ray	2.551 (90)	2.547 (70)	2.486 (90)
diffraction	2.524 (88)	2.515 (70)	2.515 (70)
pattern:	2.163 (36)	2.167 (35)	2.201 (30)
<i>d</i> , Å ( <i>I</i> , %)	2.123 (24)	2.027 (55)	2.013 (50)
	2.033 (55)	1.903 (25)	1.570 (30)
	1.906 (29)		1.513 (40)
	1.574 (35)		
Sources	this work	Irwin and Peterson, 1999; Anthony <i>et al.</i> , 2003	Burns <i>et al.</i> , 1994; Anthony <i>et al.</i> , 2003

Prepublished Article



a



b

Fig. 1. Aggregates of savelievaite (1) in veinlets of Cr-bearing clinocllore (2) which crosscut massive chromitite mainly consisting of chrome spinels (3) chemically close to the border between Al,Fe-rich magnesiochromite and Cr,Fe-rich spinel; 4 – chromite, 5 – Cr-bearing pargasite. The holotype specimen. Polished section, SEM (BSE) images.

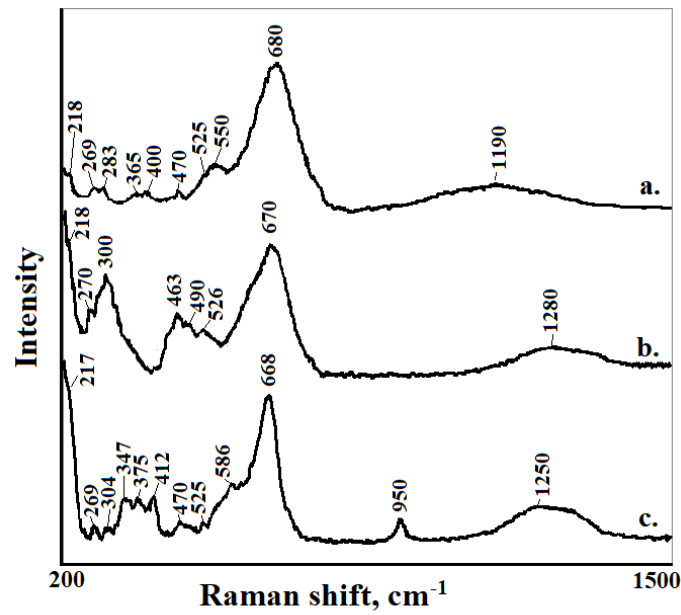
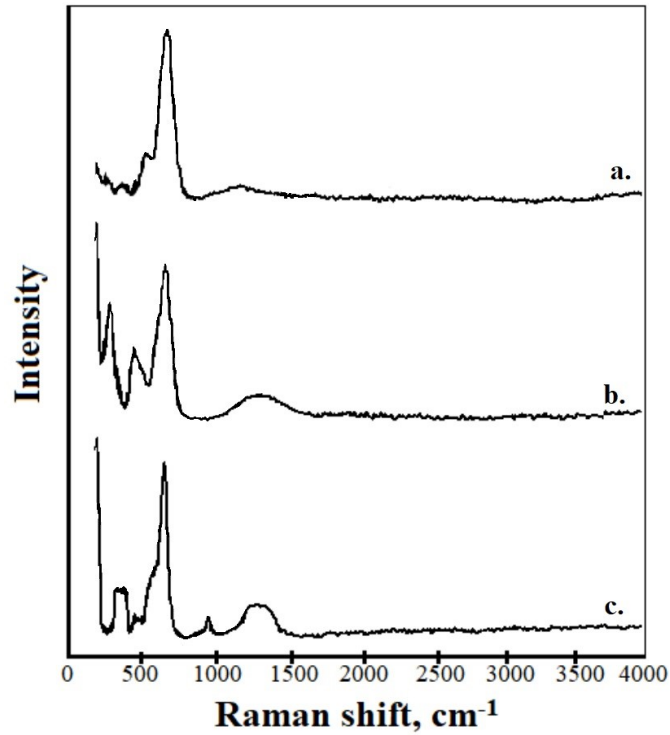


Fig. 2. The Raman spectra of (a) savelievaite, (b) common black ludwigite from the Akhmatovskaya Pit, South Urals, Russia and (c) dark green ludwigite from Gavasai, Kuraminskiy Range, Uzbekistan, chemically close to the end-member  $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ : upper figure – general view in the range 200–4000  $\text{cm}^{-1}$ , lower figure – enlargement for the range 200–1500  $\text{cm}^{-1}$ .

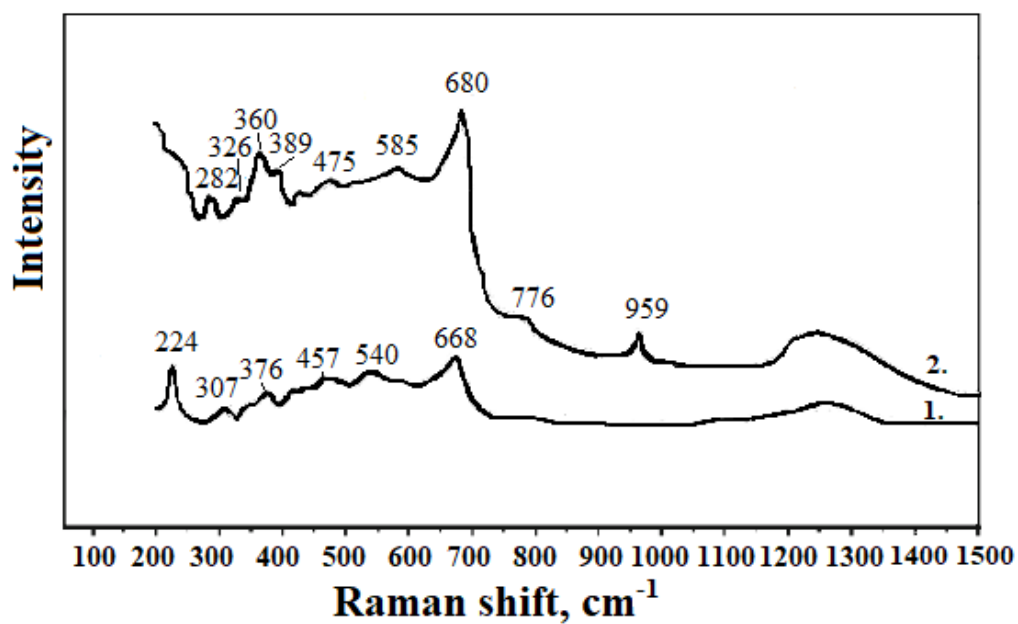


Fig. 3. The Raman spectra of (1) common ludwigite with composition  $(\text{Mg}_{1.77}\text{Fe}^{2+}_{0.23})\Sigma_{2.00}(\text{Fe}^{3+}_{0.98}\text{Al}_{0.02})\Sigma_{1.00}\text{O}_2(\text{BO}_3)$  and (2) Mg- and Al-enriched,  $\text{Fe}^{2+}$ -depleted variety of ludwigite with composition  $(\text{Mg}_{1.93}\text{Fe}^{2+}_{0.07})\Sigma_{2.00}(\text{Fe}^{3+}_{0.56}\text{Al}_{0.42}\text{Ti}_{0.01}\text{Mg}_{0.01})\Sigma_{1.00}\text{O}_2(\text{BO}_3)$  from Vysoká-Zlatno, Slovakia (after Bilohuščin *et al.*, 2017).

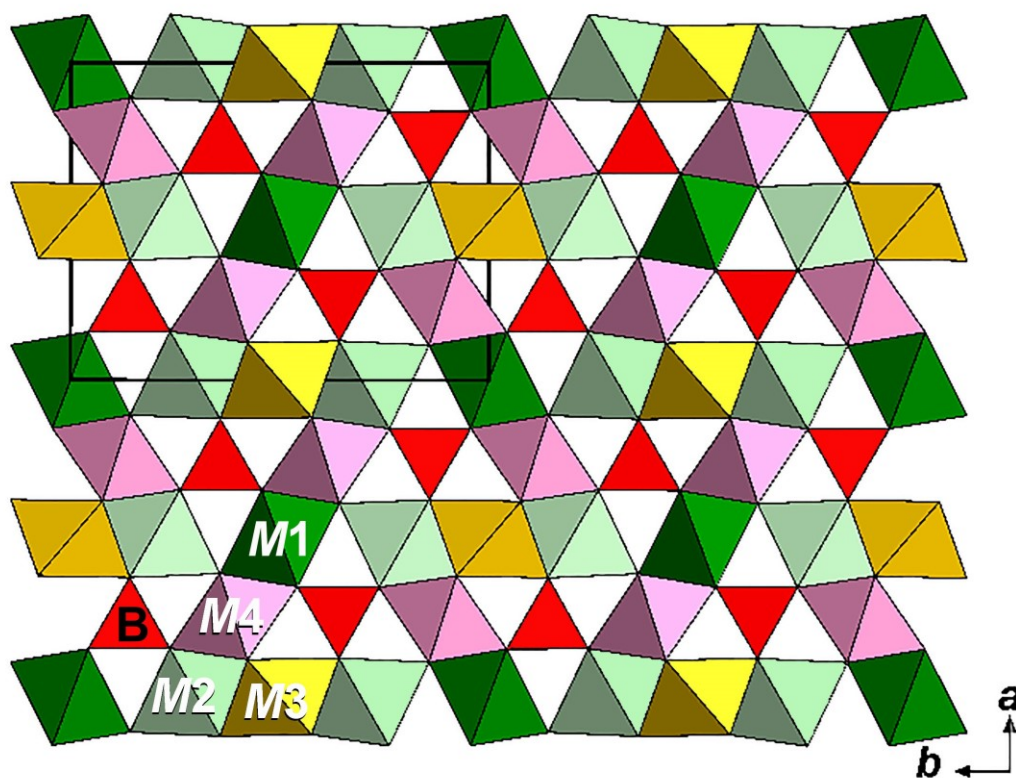


Fig. 4. The crystal structure of savelievaite. For legend see [Table 5](#). The unit cell is outlined.

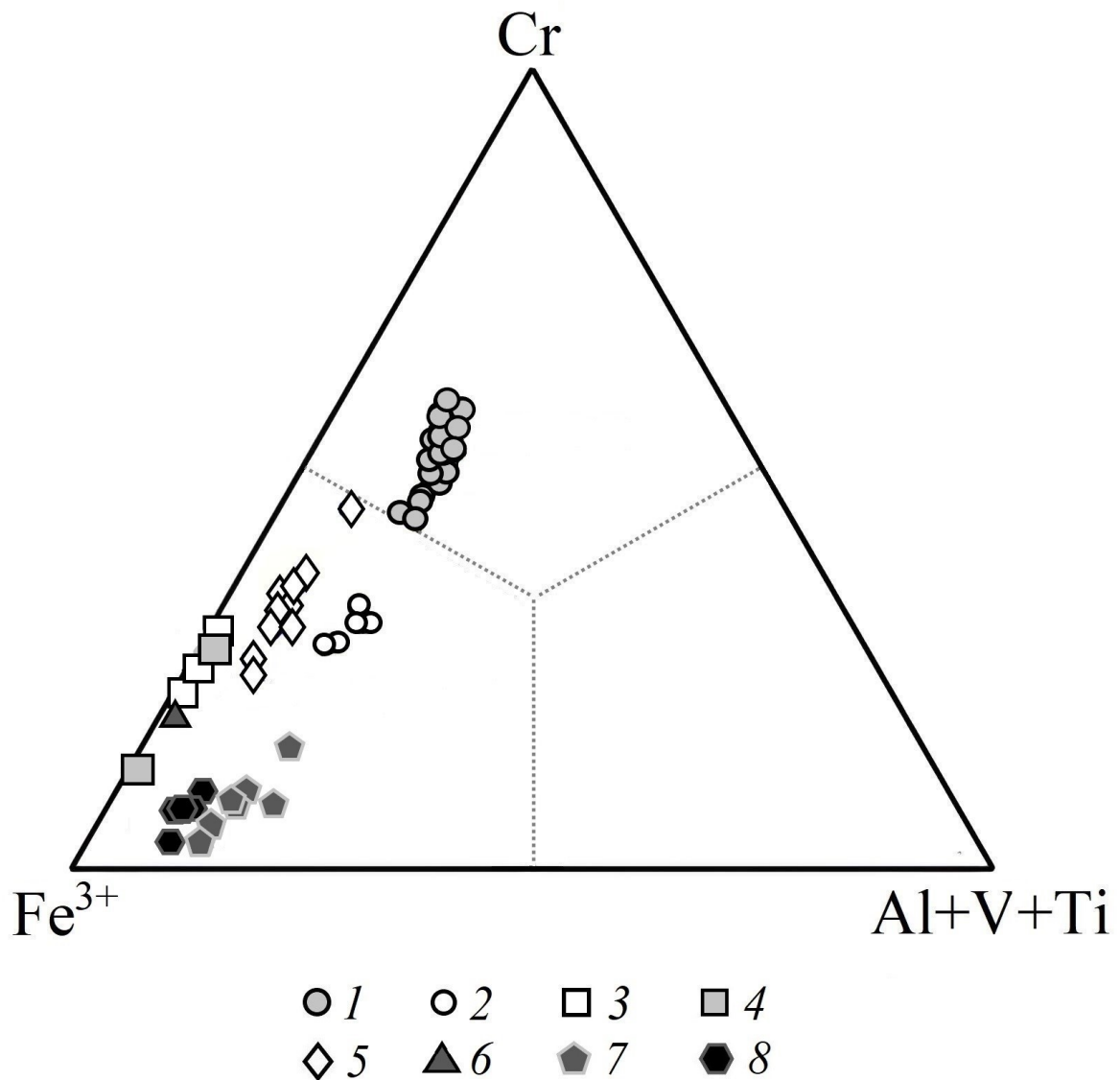


Figure 5. Relative proportions of trivalent cations and Ti in ludwigite (only samples with > 1 wt.% Cr<sub>2</sub>O<sub>3</sub> are included) and savelievaite.

1, 2 – Voikar-Syninskiy complex, Polar Urals, Russia: our data (1 – savelievaite, 2 – ludwigite); 3, 4 – Tatishchevskoe chromite deposit, South Urals, Russia (3: our data; 4: after Aleksandrov and Troneva, 2008); 5 – Volchiegorskoe chromite deposit, South Urals, Russia (after Tolkanov *et al.*, 2000); 6 – Nikolae-Maksimilianovskaya Pit, South Urals, Russia (after Aleksandrov and Troneva, 2004); 7 – Jumbo Mountain nickel deposit, Washington, USA (after Aleksandrov and Troneva, 1998, 2000); 8 – Hayama nickel mine, Fukushima Prefecture, Japan (after Kato *et al.*, 1988; Aleksandrov and Troneva, 1998).