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

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Abstract

The 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 clinocllore 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 0.05×0.4 mm, usually assembled in radiating or chaotic clusters up to 1×1.5 mm across. It is opaque, black to greenish-black. The lustre is vitreous for prismatic crystals and silky for 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, B_2O_3 16.80, Al_2O_3 2.97, V_2O_5 0.21, Cr_2O_3 21.97, Fe_2O_3 12.40, TiO_2 0.43, total 100.85. The empirical formula calculated on the basis of 5 O apfu is $(\text{Mg}_{1.72}\text{Fe}_{0.30}\text{Ni}_{0.01})_{\Sigma 2.03}(\text{Cr}_{0.57}\text{Fe}_{0.31}\text{Al}_{0.12}\text{Ti}_{0.01}\text{V}_{0.01})_{\Sigma 1.02}\text{B}_{0.96}\text{O}_5$. Savelievaite is orthorhombic, space group *Pbam*, $a = 9.2631(6)$, $b = 12.2298(8)$, $c = 3.0104(2)$ Å, $V = 341.04(4)$ Å³ and $Z = 4$. The strongest reflections of the powder X-ray diffraction pattern [$d, \text{Å}(I)(hkl)$] are: 5.101(100)(120); 2.551(90)(240); 2.524(88)(201); 2.163(36)(250); and 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, 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 Cr^{3+} content varies from 0 to 0.60 apfu. Occurrences of Cr-enriched (>1 wt.% Cr_2O_3) varieties of ludwigite are mainly related to ultrabasic complexes. The Cr-richest (>10 wt.% Cr_2O_3) ludwigite–savelievaite-series members are found in chromite ores at the Voikar–Syninskiy complex and Volchiegorskoe and Tatishchevskoe deposits, both in the South Urals.

Keywords: savelievaite; new mineral; ludwigite; magnesium chromium borate; crystal structure; chromite deposit; Voikar–Syninskiy ultrabasic complex; Urals

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Introduction

Ludwigite-related minerals form the largest structural family among natural borates. This family (or potential ludwigite supergroup) includes 16 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 16 minerals have in fact the same general formula $M_2^{2+}M^{2+-5+}\text{O}_2(\text{BO}_3)$ [$M_2^{2+}M^{3+}\text{O}_2(\text{BO}_3)$ for the majority] in which species-defining cations $M^{2+} = \text{Mg, Mn, Fe, Ni}$ and Cu ; $M^{3+} = \text{Al, Cr, Mn}$ and Fe ; $M^{4+} = \text{Ti}$; and $M^{5+} = \text{Sb}$ (Hawthorne *et al.*, 1996; Anthony *et al.*, 2003; Pasero, 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 magneesian skarns. Vonsenite, ideally $\text{Fe}_2^+\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$, is not uncommon (Aleksandrov, 1990; Grew and 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

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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 (symbol Svlv) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association. (IMA2021–051, 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 catalogue number 97680.

Savelievaite is the first borate mineral with species-defining 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 Cr^{6+} . All other minerals with both species-defining Cr and B are borosilicates of the tourmaline group.

As our, and previously published, data show, ludwigite and savelievaite form a continuous isomorphous series. The chemical variation of its members is also discussed in 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 localised 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 consists mainly of members of the magnesiochromite–chromite–(Cr,Fe)-rich spinel solid-solution system. Savelievaite and the Cr-enriched variety of ludwigite occur in clinocllore veinlets cross-cutting massive, coarse-grained chromitite (Fig. 1). These borates are associated with greenish Cr-bearing (1.5–2.5 wt.% Cr_2O_3) clinocllore 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.

In addition 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 a rhomb-like cross-section, and are 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 × 1.5 mm across. A Cr-enriched variety of ludwigite visually indistinguishable from savelievaite is also present, as similar aggregates up to 2 mm across.

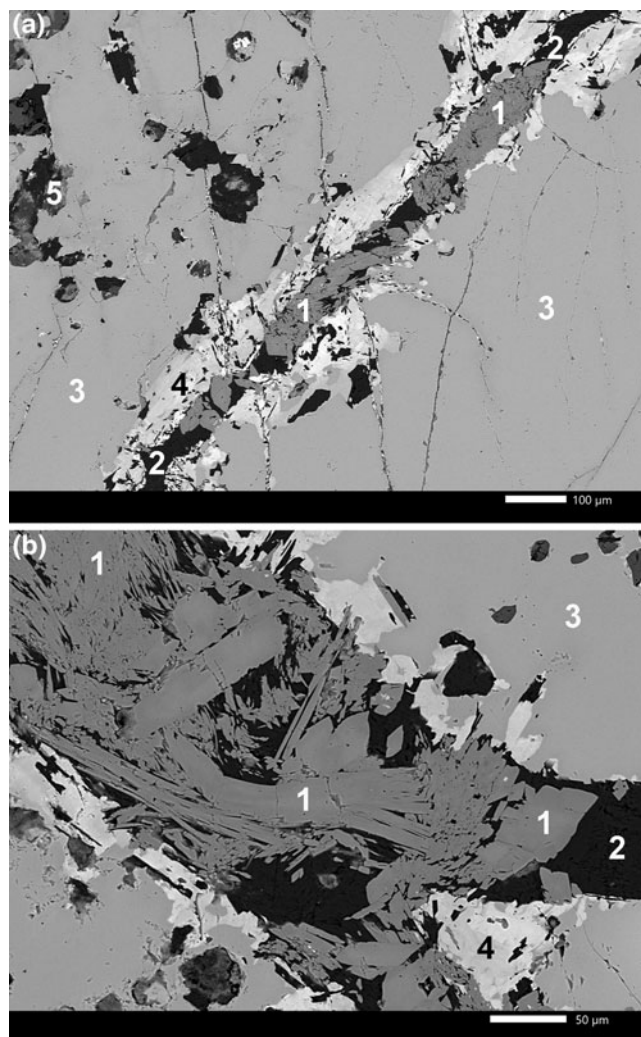


Figure 1. Aggregates of savelievaite (1) in veinlets of Cr-bearing clinocllore (2) that crosscut massive chromitite consisting mainly of chrome spinels (3) chemically close to the border between Al,Fe-rich magnesiochromite and Cr,Fe-rich spinel; 4 – chromite, 5 – Cr-bearing pargasite. The holotype specimen, catalogue number 97680. Polished section, SEM (back-scatter electron) images.

Prismatic and acicular crystals of savelievaite are opaque and black in colour, 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 g cm^{-3} . The mineral is very weakly ferromagnetic.

Under the microscope in reflected light, savelievaite is grey, pleochroism was not observed. Birefractance 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.

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

λ (nm)	R_{\max}	R_{\min}	λ (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	589	10.3	8.4
460	11.2	9.4	600	10.3	8.4
470	11.1	9.2	620	10.2	8.1
480	11.0	9.1	640	10.1	7.9
500	10.8	9.0	650	10.0	7.9
520	10.6	8.8	660	10.0	7.8
540	10.5	8.7	680	9.8	7.7
546	10.5	8.7	700	9.8	7.5

*Data for wavelengths recommended by the IMA Commission on Ore Microscopy (COM) are marked in boldtype.

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 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 $\sim 10 \mu\text{m}$. The back-scattered Raman signal was collected with $\times 40$ 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 cm^{-1} with the use a holographic diffraction grating with 1800 lines per millimetre and a resolution of 6 cm^{-1} .

For comparison, the Raman spectra of common¹ black ludwigite from the Akhmatovskaya Pit (South Urals, Russia) (Fig. 2, curve b) and dark green ludwigite from Gavasai (Kuraminskiy Range, Uzbekistan), chemically close to the end-member $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$ (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 (2009), Enholm (2016) and Bilohušćin *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 cm^{-1} corresponds to B–O antisymmetric stretching vibrations (ν_3) of triangular $(\text{BO}_3)^{3-}$ groups. The bands in the range 520–700 cm^{-1} belong to the ν_4 antisymmetric bending vibrations of B–O bonds. The series of bands between 300 and 500 cm^{-1} can be assigned to M–O stretching and bending modes. Bands with Raman shift lower than 300 cm^{-1} are interpreted as lattice modes.

A band for B–O symmetric stretching vibrations (ν_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 cm^{-1} . The absence of the ν_1 modes in Raman spectra of common ludwigite (Mg,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 Bilohušćin *et al.* (2017). In Fig. 3 the Raman spectra of two chemically different varieties of ludwigite

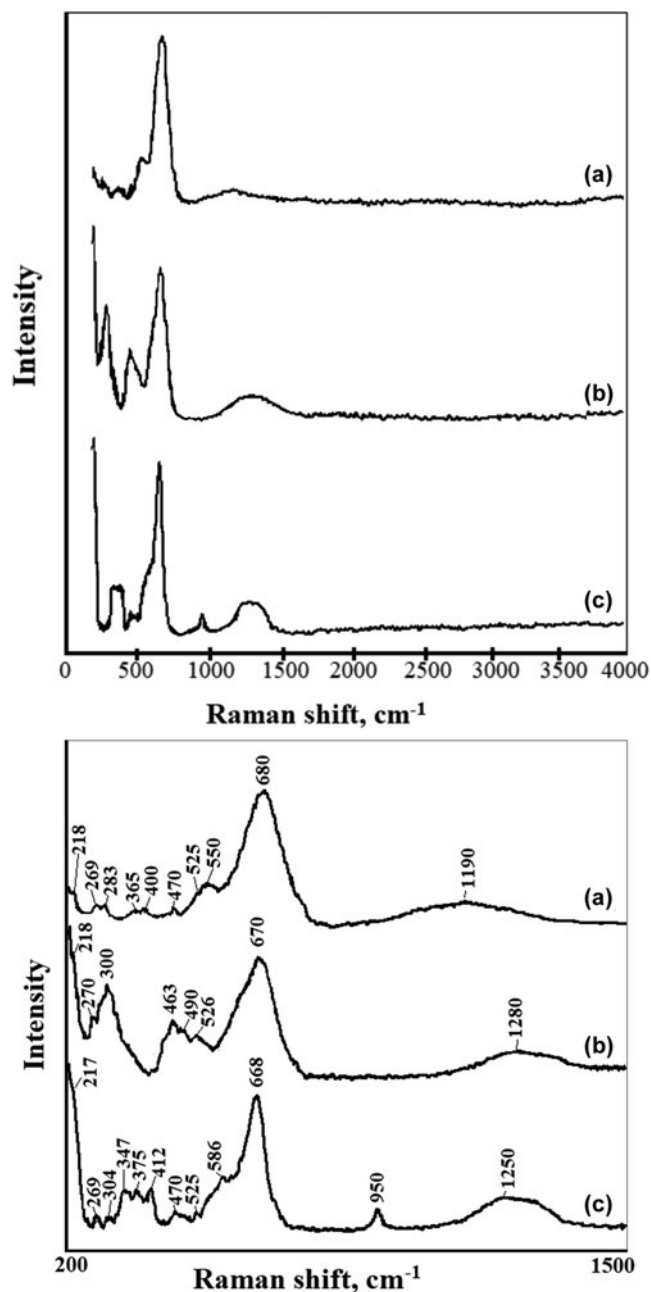


Figure 2. The Raman spectra of (a) savelievaite, (b) common black ludwigite from the Akhmatovskaya Pit, South Urals, Russia and (c) dark green ludwigite from Gavasai, Kuraminskiy Range, Uzbekistan, chemically close to the end-member $\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$: upper figure – general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

published by Bilohušćin *et al.* (2017) are shown. The band of symmetric stretching vibrations (ν_1 : 959 cm^{-1}) occurs only in the spectrum of the Mg- and Al-enriched and Fe^{2+} -depleted variety. The band corresponding to the ν_3 mode, which is characterised 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

¹The term ‘common ludwigite’ is used here to mean ludwigite with the chemical composition in the range most typical for magnesian skarns (see Aleksandrov, 1990; Aleksandrov and Troneva, 2000, 2004).

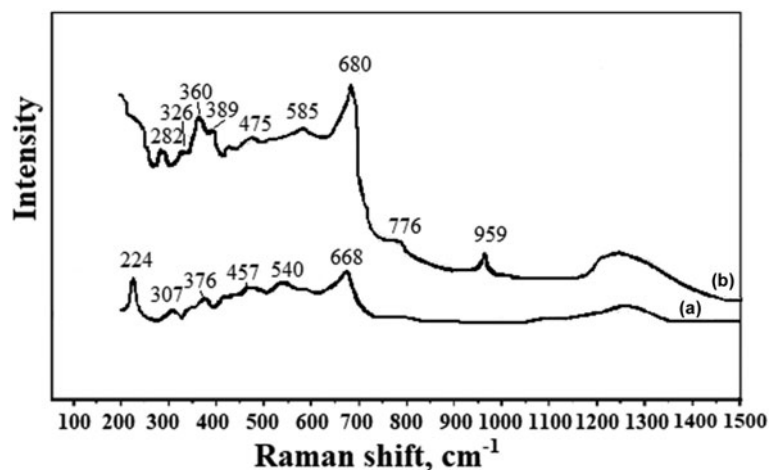


Figure 3. The Raman spectra of (a) 'common ludwigite' with composition $(\text{Mg}_{1.77}\text{Fe}_{0.23}^{2+})_{\Sigma 2.00}(\text{Fe}_{0.98}^{3+}\text{Al}_{0.02})_{\Sigma 1.00}\text{O}_2(\text{BO}_3)$ and (b) Mg- and Al-enriched, Fe^{2+} -depleted variety of ludwigite with composition $(\text{Mg}_{1.93}\text{Fe}_{0.07}^{2+})_{\Sigma 2.00}(\text{Fe}_{0.56}^{3+}\text{Al}_{0.44}\text{Ti}_{0.01}\text{Mg}_{0.01})_{\Sigma 1.00}\text{O}_2(\text{BO}_3)$ from Vysoká-Zlatno, Slovakia (after Bilohuščin *et al.*, 2017).

JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department 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 $3 \times 3 \mu\text{m}$ area. The following standards were used: MgO (Mg), Fe (Fe), Ni (Ni), LaB_6 (B), Al_2O_3 (Al), V (V), 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 (SEM) 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 μm . The following standards were used: Mg_2SiO_4 (Mg), FeS_2 (Fe), Ni (Ni), Cr (Cr) and Ti (Ti).

Representative analyses of the minerals studied 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 $(\text{Mg}_{1.72}\text{Fe}_{0.30}^{2+}\text{Ni}_{0.01})_{\Sigma 2.03}(\text{Cr}_{0.57}^{3+}\text{Fe}_{0.31}^{3+}\text{Al}_{0.12}\text{Ti}_{0.01}\text{V}_{0.01}^{3+})_{\Sigma 1.02}\text{B}_{0.96}\text{O}_5$ (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, B_2O_3 18.19, Cr_2O_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 microfocussing optics), 40 kV, 15 mA and an exposure time of 15 min. Angular resolution of the detector is 0.045 2θ (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 $V = 341.1(2)$ Å³.

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 polarisation 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 M1–3 sites were refined as Mg vs Fe, for the M4 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 $V = 345.2(9)$ Å³. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

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 BO_3 triangles. In the 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 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 an average M4–O distance of 2.027 Å (Table 6), as well as in other ludwigite-group minerals and related synthetic compounds in which the majority of 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_{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

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 ₂ O ₃	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 ₂ O ₃	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 ₂ O ₃	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 ₂ O ₃	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 ₂ O ₃	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 ₂	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 on the basis of 5 O atoms per formula unit (apfu)												
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 ²⁺	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 ²⁺	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 ³⁺	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 ^{3+,4+}	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
	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 ₂ O ₃	(17.2)	(17.4)	(17.7)	(17.5)	(17.6)	(16.3)	(17.1)	(17.6)	(17.7)	(18.3)		
Al ₂ O ₃	0.10	0.10	1.62	1.48	1.46	0.30	4.08	2.46	2.55	2.52		
V ₂ O ₃	–	–	0.20	0.17	0.24	0.10	0.09	–	–	–		
Cr ₂ O ₃	4.73	10.37	17.25	13.45	9.26	6.50	5.68	1.09	4.02	2.78		
Fe ₂ O ₃	33.79	28.57	19.20	23.40	27.50	29.80	27.11	35.12	32.45	35.16		
TiO ₂	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 on the basis of 5 O atoms per formula unit (apfu)												
Mg	1.66	1.76	1.80	1.77	1.74	1.41	1.54	1.83	1.85	1.91		
Fe ²⁺	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 ²⁺	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 ³⁺	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 ^{3+,4+}	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 Fe₂O₃ were calculated by charge balance. In analyses 11–22 boron content was not measured but calculated by stoichiometry, for 1 B apfu (calculated B₂O₃ content is given in parentheses), and the Fe²⁺:Fe³⁺ ratio was calculated by charge balance for the formula (M²⁺)₂(M^{3+,4+})₁B₁O₅; 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.

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 of the M1–O, M2–O and M3–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 Mg₂Cr³⁺O₂(BO₃), is a member of the ludwigite group, the Cr³⁺ analogue of ludwigite Mg₂Fe³⁺O₂(BO₃) and fredrikssonite Mg₂Mn³⁺O₂(BO₃) with Cr the dominant trivalent cation occupying the M4 site (Tables 5 and 7).

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

<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{calc} *	<i>d</i> _{calc} **	<i>h k l</i>	<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{calc} *	<i>d</i> _{calc} **	<i>h k l</i>
8	7.37	7	7.384	1 1 0	7	1.773	8	1.773	5 2 0
9	6.11	7	6.115	0 2 0	12	1.758	3	1.762	3 4 1
100	5.101	100	5.103	1 2 0			13	1.758	4 2 1
5	3.729	3	3.731	1 3 0			2	1.757	2 5 1
4	3.057	3	3.057	0 4 0	5	1.717	3	1.717	1 7 0
24	3.008	24	3.010	0 0 1	3	1.701	3	1.701	3 6 0
		10	2.994	3 1 0	7	1.661	10	1.660	1 6 1
8	2.904	6	2.903	1 4 0	7	1.585	6	1.586	2 6 1
10	2.788	10	2.788	1 1 1	25	1.574	35	1.574	4 4 1
10	2.756	13	2.756	3 2 0	20	1.529	9	1.529	0 8 0
7	2.701	7	2.701	0 2 1			20	1.528	5 2 1
90	2.551	98	2.552	2 4 0	22	1.506	3	1.508	1 8 0
88	2.524	100	2.524	2 0 1			32	1.505	0 0 2
13	2.336	8	2.343	1 3 1	23	1.492	33	1.491	1 7 1
		11	2.333	2 2 1	8	1.479	8	1.481	3 6 1
5	2.318	7	2.316	4 0 0			4	1.477	5 5 0
2	2.274	1	2.275	4 1 0	17	1.472	23	1.471	5 3 1
36	2.163	35	2.163	2 5 0	3	1.445	5	1.444	1 2 2
17	2.147	7	2.146	2 3 1	2	1.403	2	1.402	5 4 1
		12	2.145	0 4 1	14	1.378	23	1.378	6 4 0
24	2.123	29	2.123	3 1 1			3	1.374	6 0 1
55	2.033	67	2.033	3 2 1	3	1.364	5	1.363	0 8 1
15	1.992	14	1.991	1 6 0	3	1.348	4	1.349	1 8 1
6	1.947	9	1.946	2 4 1			1	1.345	3 1 2
29	1.906	36	1.906	3 3 1	3	1.321	3	1.321	3 2 2
6	1.866	7	1.866	2 6 0	4	1.307	5	1.308	2 8 1
2	1.845	1	1.846	4 4 0			2	1.306	6 5 0
3	1.834	2	1.836	4 0 1					
		1	1.832	5 1 0					

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

A compound isostructural with ludwigite, Ni₂²⁺Cr³⁺O₂(BO₃) [orthorhombic, *Pbam*, *a* = 9.209(1), *b* = 12.121(1), *c* = 2.9877(3) Å and *V* = 333.49(6) Å³] has been synthesised (Norrestam *et al.*,

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

Crystal data	
Crystal system, space group, <i>Z</i>	Orthorhombic, <i>Pbam</i> , 4
Unit-cell dimensions (Å)	<i>a</i> = 9.2631(6) <i>b</i> = 12.2298(8) <i>c</i> = 3.0104(2)
<i>V</i> (Å ³)	341.04(4)
Crystal size (mm)	0.02 × 0.03 × 0.06
Data collection	
Diffractometer	Xcalibur S CCD
Radiation and wavelength (Å)	MoKα; 0.71073
Temperature (K)	293(2)
Absorption correction	multi-scan
θ range for data collection (°)	2.758–28.249
Index ranges	−12 ≤ <i>h</i> ≤ 10 −16 ≤ <i>k</i> ≤ 15 −4 ≤ <i>l</i> ≤ 3
Reflections collected	2427
Independent reflections	496 (<i>R</i> _{int} = 0.0731)
Independent reflections with <i>I</i> > 2σ(<i>I</i>)	410
Refinement	
Refinement method	full-matrix least-squares on <i>F</i> ²
Number of refined parameters	62
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ * = 0.0427
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0589, <i>wR</i> ₂ * = 0.0459
GoF	0.990
Largest diff. peak and hole (e [−] /Å ³)	0.50 [1.50 Å from O4] −0.57 [1.71 Å from O3]

**w* = 1/[σ²(*F*_o) + (0.0055*P*)²]; *P* = {[max of (0 or *F*_o)] + 2*F*_o}/3

Table 5. Coordinates and equivalent displacement parameters (*U*_{eq}, in Å²) of atoms and site occupancy factors (s.o.f.) for savelievaite.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	s.o.f.
M1	0.0	0.0	½	0.0052(7)	Mg _{0.959(6)} Fe _{0.041(6)}
M2	0.00053(17)	0.27911(12)	½	0.0050(5)	Mg _{0.973(5)} Fe _{0.027(5)}
M3	½	0.0	0.0	0.0072(5)	Mg _{0.644(7)} Fe _{0.356(7)}
M4	0.24039(9)	0.11370(6)	0.0	0.0033(3)	'Cr _{0.810(11)} Al _{0.190(11)} '*
B	0.2715(6)	0.3605(5)	0.0	0.0103(12)	B _{1.00}
O1	0.3480(3)	0.4572(3)	0.0	0.0102(8)	O _{1.00}
O2	0.1103(3)	0.1428(3)	½	0.0109(8)	O _{1.00}
O3	0.1228(3)	0.3580(3)	0.0	0.0114(8)	O _{1.00}
O4	0.3823(3)	0.0768(3)	½	0.0122(9)	O _{1.00}
O5	0.3465(4)	0.2622(3)	0.0	0.0102(9)	O _{1.00}

*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 *n*_{ref} = 21.91.

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.% Cr₂O₃) is not very rare in ludwigite (Aleksandrov and Troneva, 1998, 2000), however varieties of this mineral containing as much as several wt.% Cr₂O₃ have been described from only a few localities. A ludwigite variety containing up to 4.0 wt.% Cr₂O₃ 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 the first electron microprobe analyses of Cr-enriched ludwigite from the Hayama mine (up to 2.9 wt.% Cr₂O₃), from altered dunite of the Jumbo Mountain nickel deposit, Snohomish Co., Washington, USA (up to 5.7 wt.% Cr₂O₃; Aleksandrov and Troneva, 1998, 2000), from calciphyre of the Nikolae–Maksimilianovskaya Pit, Zlatoust District, South Urals, Russia (6.5 wt.% Cr₂O₃; Aleksandrov and Troneva, 2004), and from the Tatishchevskoe deposit (up to 10.4 wt.% Cr₂O₃, though without a 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.% Cr₂O₃ that corresponds to 0.45 apfu Cr³⁺ (Tolkanov *et al.*, 2000).

Table 6. Selected interatomic distances (Å) in the structure of savelievaite.

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

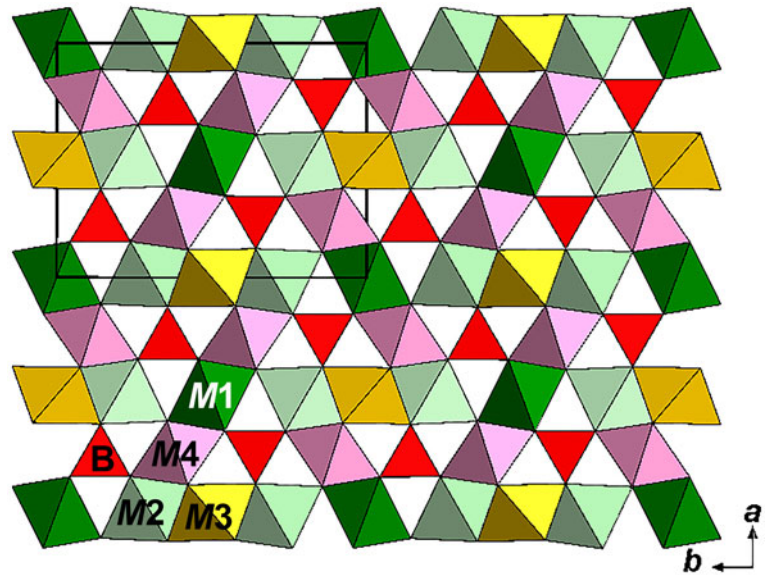


Figure 4. The crystal structure of savelievaite. For occupancies see Table 5. The unit cell is outlined. Drawn using the program *Diamond*, version 3.2k.

Chromium-bearing ludwigite has also been mentioned from chromite deposits related to the Khadatskiy basite–ultrabasic massif in the Polar Urals and the Verblyuzhiegorsky ultrabasic massif in the South Urals, both Russia. In ludwigite from these localities, up to 5–7 wt.% Cr_2O_3 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'nitskiy (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 selections 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_2O_3 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^{3+} content ranges from 0 to 0.60 apfu, corresponding to 0–23 wt.% Cr_2O_3 . The main variable value in this series is the $\text{Fe}^{3+}:\text{Cr}$ ratio, Al plays subordinate but perceptible role whereas

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	Orthorhombic	Orthorhombic
Space group	<i>Pbam</i>	<i>Pbam</i>	<i>Pbam</i>
Unit cell data:			
<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 ³)	341.04 (2)	343	341.7
<i>Z</i>	4	4	4
Strongest lines of the powder	5.101 (100) 3.008 (24)	5.12 (100) 2.990 (25)	5.16 (80) 2.590 (100)
X-ray diffraction pattern:	2.551 (90) 2.524 (88)	2.547 (70) 2.515 (70)	2.486 (90) 2.515 (70)
<i>d</i> , Å (<i>l</i> , %)	2.163 (36) 2.123 (24) 2.033 (55) 1.906 (29) 1.574 (35)	2.167 (35) 2.027 (55) 1.903 (25)	2.201 (30) 2.013 (50) 1.570 (30) 1.513 (40)
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)

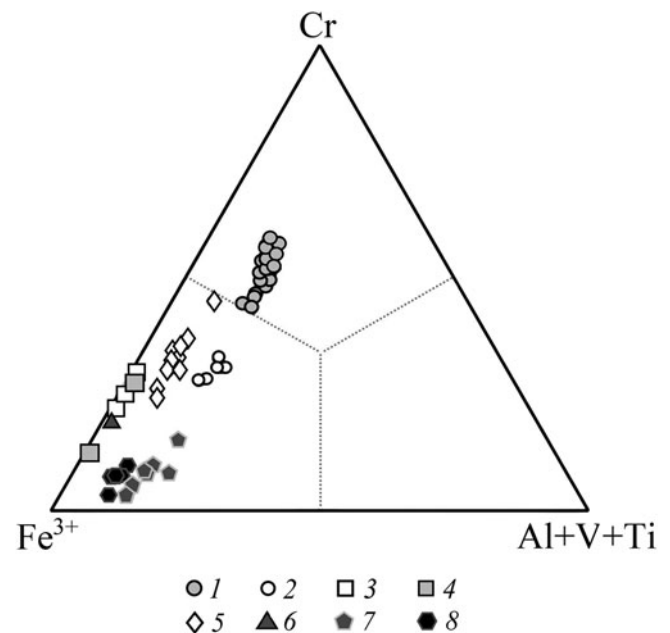


Figure 5. Relative proportions of trivalent cations and Ti in ludwigite (only samples with > 1 wt.% Cr_2O_3 are included) and savelievaite. 1, 2 – Voikar–Syninskiy complex, Polar Urals, Russia: our data (1 – savelievaite, 2 – ludwigite); 3, 4 – Tatishchevskoe chromite deposit, South Urals, Russia (3: 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).

other $M^{3+,4+}$ cations (V and Ti) seem insignificant. All the samples plotted in Fig. 5 have 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 analysed minerals belonged to the ludwigite group and that these solid solutions constitute a true isomorphous series. The synthesis of $Ni_2^{2+}Cr^{3+}O_2(BO_3)$, 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 mineralisation form in separate geological settings. However, in some cases the ‘geochemical ways’ of these elements cross with the resulting 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 crystallise. Except for the Nikolae–Maksimilianovskaya Pit at the 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.% Cr_2O_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 Tatishchevskoe chromium deposits, the borate mineralisation 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, in addition to ultrabasic rocks, only gabbroid dykes occur near the savelievaite locality, and we cannot suggest a geochemically substantiated source of boron.

Supplementary material. The supplementary material for this article can be found at [<https://doi.org/10.1180/mgm.2024.39>].

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Competing interests. The authors declare none.

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