Title

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Article

Ferrotorryweiserite, $Rh_5Fe_{10}S_{16}$, a new mineral from the Sisim placer zone, eastern Sayans, Russia, and a note on the torryweiserite–ferrotorryweiserite series

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Abstract: Ferrotorryweiserite, $Rh_5Fe_{10}S_{16}$, is present as small grains (≤ 20 μm), portions of droplet-like inclusions (up to 50 μm in diameter) of platinum-group minerals (PGM), in association with oberthürite or pentlandite enriched in Rh, laurite and isoferroplatinum (or Fe-rich platinum), hosted by placer grains of Os-Ir alloy (≤ 0.5 mm) in the River Ko deposit. The latter is a part of the Sisim placer zone derived likely from ultramafic units of the Lysanskiy layered complex, southern Krasnoyarskiy kray, Russia. It is opaque, gray to brownish gray in reflected light, very weakly bireflectant, nonpleocroic to slightly pleochroic (grayish to light brown tints), and weakly anisotropic. The calculated density is 5.93 g·cm^{-3}. Mean results (and ranges) of four WDS analyses are: Ir 18.68 (15.55 – 21.96), Rh 18.34 (16.32 – 20.32), Pt 0.64 (0.19 – 1.14)**,** Ru 0.03 (0.00 – 0.13), Os 0.07 (0.02 – 0.17), Fe 14.14 (13.63 – 14.64), Ni 13.63 (12.58 – 14.66), Cu 4.97 (3.42 – 6.41), Co 0.09 (0.07 – 0.11), S 29.06 (28.48 – 29.44), and total 99.66 wt.%. They correspond to the following formula calculated for a total of 31 atoms per formula unit: $(Rh_{3.16}Ir_{1.72}Pt_{0.06}Ru_{0.01}Os_{0.01})_{\Sigma 4.95}(Fe_{4.48}Ni_{4.11}Cu_{1.38}Co_{0.03})_{\Sigma 10.00}S_{16.05}$. Results of synchrotron micro-Laue diffraction studies indicate that ferrotorryweiserite is trigonal; its probable space group is $R\bar{3}m$ (#166).

The unit-cell parameters refined from 177 reflections are: *a* = 7.069 (2) Å, *c* = 34.286 (11) Å, *V* = 1484 (1) Å^3, and Z = 3. The *c*:*a* ratio is 4.8502. The strongest eight peaks in the X-ray diffraction pattern [*d* in Å(*hkil*)(I)] are: 2.7950 (2 0 -2 5) (100); 5.7143 (0006) (60); 1.7671 (2 2 -4 0) (44.4); 3.0486 (2 0 -2 1) (39.4); 5.7650 (1 0 -1 2) (38.6); 2.5956 (2 0 -2 7) (37.8); 3.0058 (1 1 -2 6) (36.5); and 1.5029 (4 -2 -2 12) (35.3). Ferrotorryweiserite and associated PGM formed from microvolumes of residual melt at late stages of crystallization of grains of Os-dominant alloy in lode zones of chromitites of the Lysanskiy complex. The name ferrotorryweiserite indicates that it represents the Fe-dominant analogue of torryweiserite. We also report occurrences of ferrotorryweiserite in the Marathon deposit, Coldwell Complex, Ontario, Canada, and infer the existence torryweiserite–ferrotorryweiserite solid solution in other deposits and complexes.

Keywords: Ferrotorryweiserite; torryweiserite–ferrotorryweiserite solid solution; platinum-group mineral; PGE sulfide; rhodium–iron sulfide; Sisim placer zone; River Ko deposit; Lysanskiy layered complex; Eastern Sayans; Russia

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1. Introduction

Ferrotorryweiserite, $Rh_5Fe_{10}S_{16}$, is a new mineral species discovered in the River Ko suite which represents a part of the Sisim placer zone south of Krasnoyarsk, Krasnoyarskiy kray, Russia [approximate location 54° 45' N, 93° 09' E]. The mineral and its name were approved (IMA 2021-055) by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association [1]. Our aims are to describe its properties and to report, with the involvement of literature sources, on the existence of solid-solution series that extends from ferrotorryweiserite toward torryweiserite, $Rh_5Ni_{10}S_{16}$, discovered in the Marathon Cu–Pd deposit, Coldwell complex, Ontario, Canada [2-4]. Ferrotorryweiserite is also related to tamuraite, $Ir_5Fe_{10}S_{16}$, and kuvaevite, $Ir_5Ni_{10}S_{16}$ [5, 6], other members of the torryweiserite family which occur as inclusions in grains of Os-Ir alloy in heavy-mineral fractions of platinum-group minerals (PGM) in the placer zone formed by the Sisim river and its trubutaries, rivers Ko and Seyba [7, 8] at the expense of ultramafic units of the Lysanskiy layered complex, eastern Sayans, south-central Siberia [9]. Further occurrences of members of the ferrotorryweiserite–torryweiserite series are expected in relation to a variety of ore deposits associated with ultrabasic-basic complexes known as sources of Rh- and Ir-based species of PGM, cf. [10, 11].

2. Materials and Methods

Our materials involved hundreds grains of Os-Ir alloy minerals examined from the placer suite at river Ko of the Sisim zone. In some of these grains, ferrotorryweiserite occurs in composite inclusions with other PGM hosted by the osmium enriched in Ir.

Electron-microprobe analyses of ferrotorryweiserite were done at McGill University by means of wavelength spectrometry (WDS) using a JEOL JXA 8900L facility operated at 20 kV, 20 nA, with a beam diameter set at 3 μm. The following X-ray lines were used: Cu*L*α, Ni*K*α, Fe*K*α, Co*K*α, Ir*L*α, Rh*L*α, Pt*L*α, Pd*L*β, Os*M*α, Ru*L*α and S*K*α. Counting times were 20 s on peak. The Phi-Rho-Z method of corrections was applied. The peak-overlap corrections included Fe → Co, Os → Ir, Ru → Pd, Ir → Pt, and Ru → Rh corrections. The standards used were pure metals for the platinum-group elements (PGE), Fe, Cu, Co, and pentlandite for Ni and S). Values of standard deviations (σ) are ≤ 0.2 for Ir, Pt, and Cu, ≤ 0.1 for Ru, Os, Fe, and Ni, and ≤ 0.05 for Rh,Co and S.

Synchrotron micro-Laue diffraction studies, followed by monochromator energy scans, were performed on the holotype specimens of ferrotorryweiserite from River Ko at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory, Berkeley, California, USA. The Laue diffraction patterns were collected using a PILATUS 1M area detector in reflection geometry. The patterns were analyzed and indexed using XMAS v.6 after Tamura, 2014 [12].

3. Results and Observations

3.1. Appearance, properties and morphology

Ferrotorryweiserite occurs as small grains (≤ 20 μm; Figure 1a, b), which are portions of composite, droplet-like inclusions (typically up to 50-70 μm in diameter) of PGM, mainly oberthürite or pentlandite enriched in Rh, laurite and isoferroplatinum or Fe-rich platinum, hosted by placer grains of Os-Ir alloy (≤ 0.5 mm across). In general, the PGM assemblage investigated is dominated by Os-Ir-Ru alloys, where osmium is a major species, and iridium is subordinate. Rutheniridosmine is rare. The compositional field is limited to the Ru-poor portion of the system Os–Ir–Ru by the line Ru:Ir = 1 in the entire Sisim – Ko – Seyba placer area [9]. In addition, ferrotorryweiserite occurs in the Marathon deposit, Coldwell Complex, Ontario, Canada, in association with torryweiserite and oberthürite, $Rh_3(Ni,Fe)_{32}S_{32}$ [3].

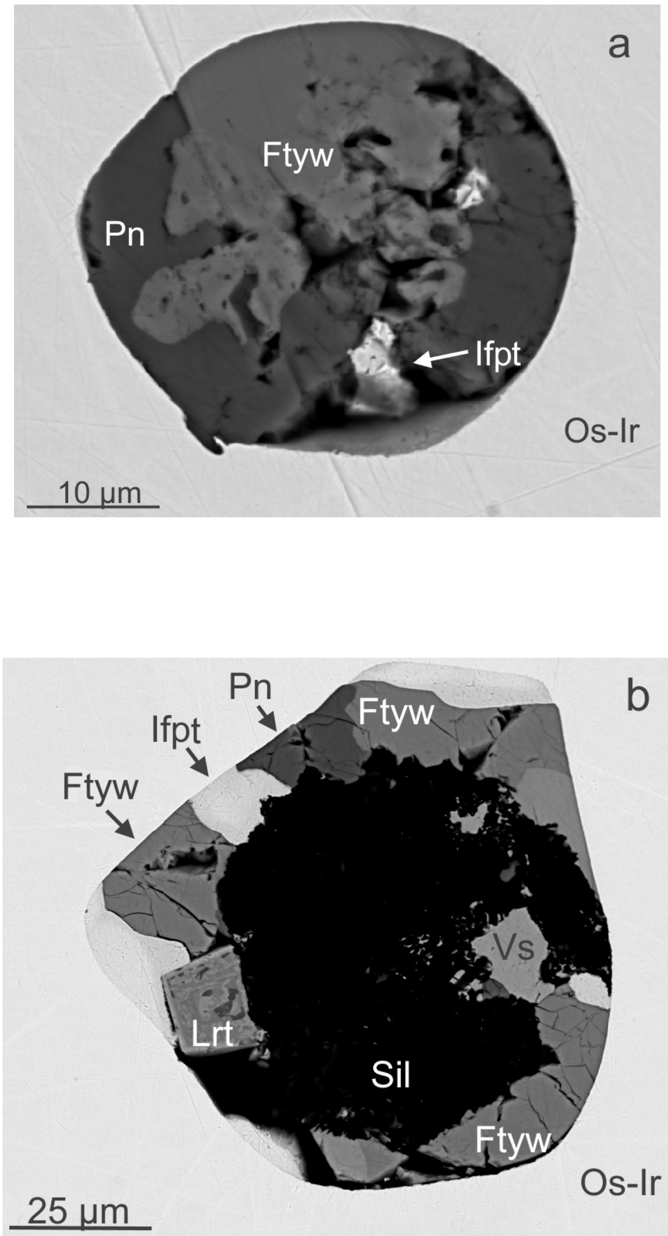

Figure 1 (a, b). Back-scattered electron images showing droplet-like inclusions of platinum-group minerals, hosted by placer grains of Os-Ir alloy labeled Os-Ir (i.e., native osmium enriched in Ir), in which ferrotorryweiserite (Ftyw) is associated with a Rh-rich pentlandite or oberthürite (Pn), isoferroplatinum (Ifpt), a vasilite-like phase (Vs), heterogeneous grain of laurite (Lrt), and a fine mixture of hydrous silicates (Sil).

The observed habit of ferrotorryweiserite grains is anhedral; other forms or evidence for twinning were not observed. The *c*:*a* ratio calculated from the unit cell parameters is 4.8502.

In reflected light, grains of ferrotorryweiserite are gray to brownish gray. Bireflectance is very weak to absent. The mineral is non-pleochroic or slightly pleochroic (gray to light brown tints). It is weakly anisotropic (gray to light yellow tints). Internal reflections were not observed; reflectance values could not be measured because of insufficient grain-sizes. Also, its streak was not observed because of insufficient grain-sizes. The mineral is opaque; its lustre is metallic. Fluorescence and tenacity could not be evaluated, and values of hardness (Mohs or micro-indentation) could not be measured owing to the small grain-size. Cleavage or fracture were not observed.

Density could not be measured due to the small grain-size. The calculated value of density is 5.93 $g \cdot cm^{-3}$, which is based on the unit-cell volume from diffraction measurements by means of synchrotron radiation and the empirical formula.

3.2. Chemical composition and formula

Mean results of electron-microprobe analyses of ferrotorryweiserite, based on four data-points (Table 1), correspond to the following formula calculated on the basis of a total of 31 atoms per formula unit (*apfu*) by analogy and according to the structure of the Ni-dominant analogue, i.e., torryweiserite [3]: $(Rh_{3.16}Ir_{1.72}Pt_{0.06}Ru_{0.01}Os_{0.01})_{\Sigma 4.95}(Fe_{4.48}Ni_{4.11}Cu_{1.38}Co_{0.03})_{\Sigma 10.00}S_{16.05}$. The simplified formula is $(Rh,Ir)_5(Fe,Ni,Cu)_{10}S_{16}$. Consequently, the ideal formula is $Rh_5Fe_{10}S_{16}$, which requires Rh 32.44, Fe 35.21, and S 32.34, total 100 wt.%. Compositional variations documented in the ferrotorryweiserite – torryweiserite series in the River Ko placer area are presented in Table 2.

The average of four WDS data-points, performed on specimens of ferrotorryweiserite from the Marathon deposit, Coldwell complex, Ontario, Canada, is consistent: $(Rh_{4.59}Ir_{0.11}Pt_{0.06})_{\Sigma 4.76}(Fe_{4.62}Ni_{3.58}Cu_{1.66}Co_{0.39})_{\Sigma 10.24}S_{15.99}$. A total value of all metals is notably stoichiometric (15.00 *apfu*) in this formula. Thus, a minor amount of a Fe-site cation is presumably present at the Rh site.

Table 1. Chemical data for ferrotorryweiserite from the River Ko placer deposit.

Constituent	Mean (wt.%)	Range (wt.%)
Cu	4.97	3.42 – 6.41
Ni	13.63	12.58 – 14.66
Fe	14.14	13.63 – 14.64
Co	0.09	0.07 – 0.11
Ir	18.68	15.55 – 21.96
Rh	18.34	16.32 – 20.32
Pt	0.64	0.19 – 1.14
Os	0.07	0.02 – 0.17
Ru	0.03	0.00 – 0.13
S	29.06	28.48 – 29.44
Total	99.66	

Table 2. Compositions of members of the ferrotorryweiserite – torryweiserite series from the River Ko placer area

#	S	Fe	Co	Ni	Cu	Ru	Rh	Ir	Os	Pt	Total, wt.%
1	28.61	14.17	0.10	14.85	3.50	0.00	16.36	21.87	0.04	0.24	99.75
2	28.48	14.64	0.09	14.66	3.65	0.00	16.32	21.96	0.02	0.19	100.02
3	28.96	14.33	0.11	14.54	3.42	0.00	16.78	21.46	0.02	0.30	99.91
4	29.44	13.63	0.07	12.58	6.41	0.00	19.96	15.55	0.17	1.14	98.96
5	29.38	13.97	0.07	12.74	6.40	0.13	20.32	15.75	0.07	0.94	99.77
6	31.20	13.58	0.12	18.74	2.62	0.01	29.32	4.24	0.00	0.11	99.95
7	30.81	13.43	0.14	18.74	2.53	0.04	29.40	4.50	0.00	0.24	99.83
8	30.69	13.33	0.12	18.95	2.18	0.03	28.99	4.30	0.03	0.34	98.95
9	31.00	13.23	0.12	18.49	1.90	0.32	30.99	4.00	0.00	0.04	100.09
10	31.06	13.40	0.11	18.88	2.29	0.04	29.65	4.45	0.00	0.35	100.23
11	28.78	12.31	0.09	15.66	4.04	0.07	16.76	20.83	0.03	0.88	99.45
12	28.31	12.45	0.09	16.20	3.77	0.06	16.61	20.65	0.07	0.79	99.00
13	27.95	12.09	0.08	16.08	3.80	0.05	16.49	20.93	0.06	1.09	98.63
14	30.68	13.20	0.13	18.46	2.15	0.44	30.14	4.191	0.00	0.15	99.53
15	28.80	9.70	0.05	16.37	7.15	0.03	17.93	17.94	0.04	1.91	99.92
16	28.59	9.56	0.05	16.36	6.80	0.02	17.58	17.89	0.08	2.04	98.95
17	29.97	13.63	0.04	14.60	6.43	0.05	23.97	10.58	0.01	0.75	100.03
18	30.00	13.09	0.05	14.85	6.30	0.01	23.93	10.57	0.00	0.62	99.42

***Apfu* (calculated on the basis of a total of 31 apfu)**

#	S	Fe	Co	Ni	Cu	Ru	Rh	Ir	Os	Pt	ΣPGE	Σ(Fe,Ni, Cu,Co)	ΣMe
1	15.99	4.55	0.03	4.53	0.99	0.00	2.85	2.04	0.00	0.02	4.91	10.10	15.01
2	15.89	4.69	0.03	4.47	1.03	0.00	2.84	2.04	0.00	0.02	4.90	10.21	15.11
3	16.10	4.57	0.03	4.41	0.96	0.00	2.91	1.99	0.00	0.03	4.92	9.98	14.90
4	16.17	4.30	0.02	3.77	1.78	0.00	3.42	1.42	0.02	0.10	4.96	9.87	14.83
5	16.04	4.38	0.02	3.80	1.76	0.02	3.46	1.43	0.01	0.08	5.00	9.96	14.96
6	15.99	4.00	0.03	5.25	0.68	0.00	4.68	0.36	0.00	0.01	5.06	9.95	15.01
7	15.90	3.98	0.04	5.28	0.66	0.01	4.73	0.39	0.00	0.02	5.14	9.96	15.10
8	15.94	3.97	0.04	5.38	0.57	0.01	4.69	0.37	0.00	0.03	5.10	9.96	15.06
9	15.98	3.91	0.03	5.20	0.49	0.05	4.98	0.34	0.00	0.00	5.38	9.65	15.02
10	15.96	3.95	0.03	5.30	0.59	0.01	4.75	0.38	0.00	0.03	5.16	9.88	15.04
11	16.12	3.96	0.03	4.79	1.14	0.01	2.92	1.95	0.00	0.08	4.97	9.92	14.88
12	15.95	4.02	0.03	4.98	1.07	0.01	2.92	1.94	0.01	0.07	4.95	10.11	15.05
13	15.91	3.95	0.03	5.00	1.09	0.01	2.92	1.99	0.01	0.10	5.03	10.07	15.09
14	15.92	3.93	0.04	5.23	0.56	0.07	4.87	0.36	0.00	0.01	5.32	9.76	15.08
15	15.99	3.09	0.02	4.96	2.00	0.01	3.10	1.66	0.00	0.17	4.94	10.07	15.01
16	16.03	3.08	0.01	5.01	1.92	0.00	3.07	1.67	0.01	0.19	4.94	10.02	14.97
17	15.91	4.15	0.01	4.23	1.72	0.01	3.96	0.94	0.00	0.07	4.97	10.12	15.09
18	15.99	4.00	0.01	4.32	1.69	0.00	3.97	0.94	0.00	0.05	4.97	10.03	15.01

Note: These results of WDS analyses are listed in weight%, and values of atoms per formula unit (apfu) are based on a total of thirty one atoms per formula unit (apfu). Zerro means "not detected". Numbers 1 – 5 pertain to ferrotorryweiserite, and #6 – 18 correspond to torryweiserite.

Table 3. Compositions of potential members of the ferrotorryweiserite – torryweiserite series from other localities

	Marathon				Tulameen	Yubdo				Miass	
wt.%	1	2	3	4	5	6	7	8	9	10	Mean
S	32.63	31.38	30.49	31.82	30.07	31.90	32.10	31.80	31.90	28.22	31.23
Fe	21.05	14.00	14.55	13.90	16.83	16.30	15.80	15.60	17.80	14.94	16.08
Co	0.75	2.20	0.66	2.10	0.00	1.01	1.09	1.11	0.80	0.00	1.22
Ni	10.17	14.57	12.51	14.45	9.96	11.50	11.60	11.60	10.10	12.52	11.90
Cu	5.75	6.44	7.12	6.64	5.78	4.71	4.34	4.05	4.71	3.32	5.29
Ru	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.04
Rh	28.77	30.39	25.59	31.65	20.95	27.20	27.40	28.20	26.50	17.14	22.07
Ag	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Ir	0.00	0.00	5.34	0.06	18.20	6.81	6.70	6.54	7.21	22.96	9.23
Os	0.00	0.00	0.00	0.05	0.15	0.00	0.00	0.00	0.00	0.00	0.10
Pt	0.21	0.19	2.13	0.33	1.24	0.96	1.20	1.05	0.70	0.00	0.89
Total, wt.%	99.36	99.17	98.39	101.00	103.22	100.39	100.23	99.95	99.72	99.10	100.05
apfu											
S	16.16	15.86	16.06	15.88	16.10	16.42	16.55	16.49	16.48	16.06	16.20
Fe	5.99	4.06	4.40	3.98	5.17	4.82	4.68	4.64	5.28	4.88	4.79
Co	0.20	0.61	0.19	0.57	0.00	0.28	0.31	0.31	0.23	0.00	0.34
Ni	2.75	4.02	3.60	3.94	2.91	3.23	3.27	3.29	2.85	3.89	3.38
Cu	1.44	1.64	1.89	1.67	1.56	1.22	1.13	1.06	1.23	0.95	1.38
Ru	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Rh	4.44	4.79	4.20	4.92	3.50	4.36	4.40	4.56	4.26	3.04	4.25
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ir	0.00	0.00	0.47	<0.01	1.63	0.59	0.58	0.57	0.62	2.18	0.83
Os	0.00	0.00	0.00	<0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Pt	0.02	0.02	0.18	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.06
Total *apfu*	31.00	31.00	31.00	31.00	30.89	30.92	30.90	30.91	30.94	31.00	31.24
ΣPGE	4.46	4.80	4.80	4.80	5.14	4.95	4.98	5.12	4.89	5.22	4.88
ΣPGE/Σ*Me*	14.84	15.14	14.89	14.97	14.79	14.50	14.35	14.43	14.47	14.94	14.71
Ni/Fe	0.46	0.99	0.99	0.99	0.56	0.67	0.70	0.71	0.54	0.80	0.74
Fe/Ni	2.18	1.01	1.22	1.01	1.78	1.49	1.43	1.41	1.85	1.25	1.51

Note: Minerals of ferrotorryweiserite composition are from the Marathon deposit, Coldwell complex, Ontario, Canada (this study and a mean WDS composition in [3], the Tulameen Alaskan-type complex, British Columbia, Canada, after Aubut, 1979 [13], the Yubdo placer deposit in Ethiopia after Evstigneeva, 1992 [14], and the Miass placer zone, southern Urals, Russia, after Barkov *et al.*, 2018 [15].

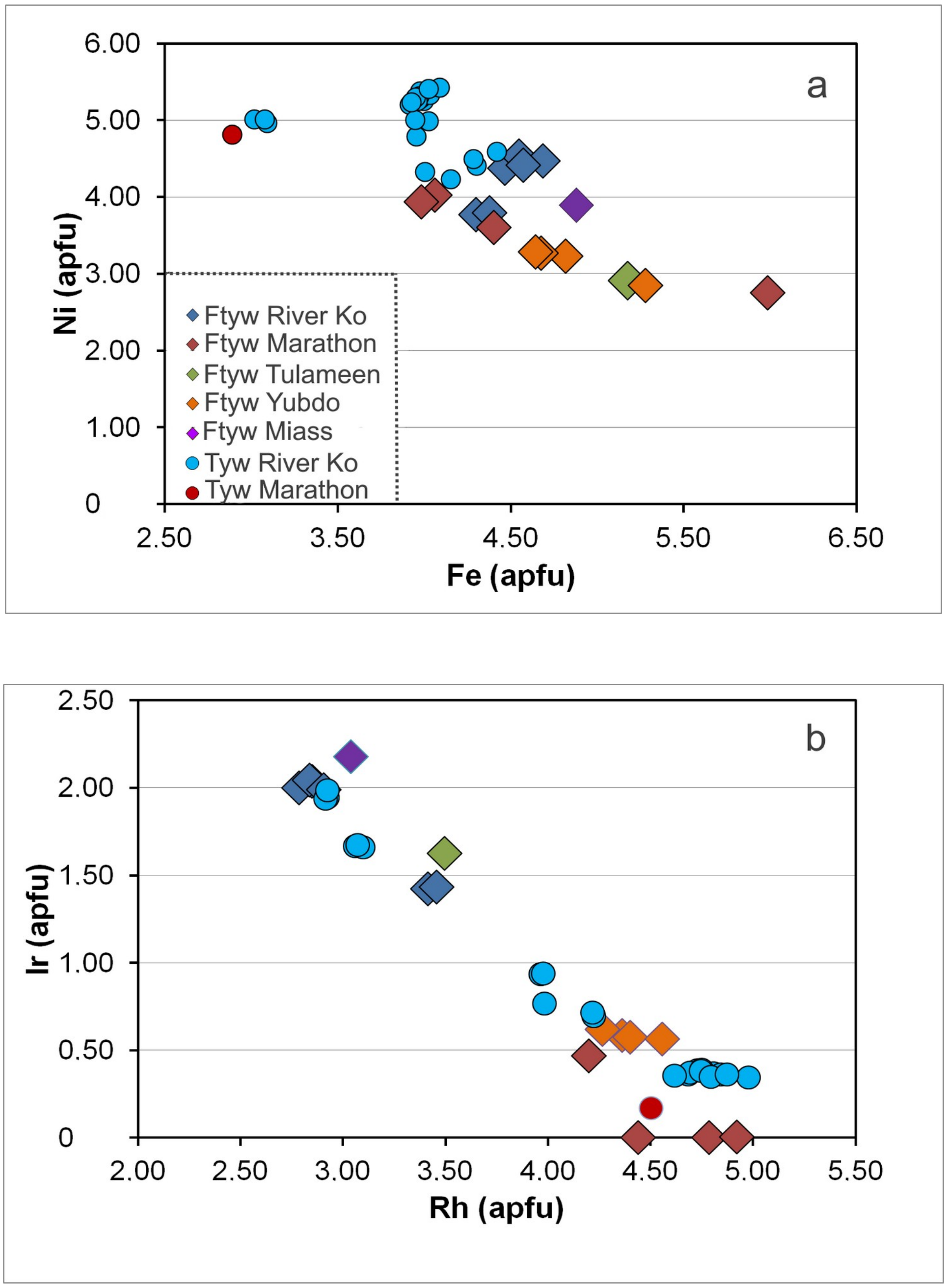

Figure 2 (a, b). Correlations of Fe vs. Ni (a) and Rh vs. Ir (b) (plotted in values of atoms per formula unit, *apfu,* calculated for a total of 31 *apfu*) which are observed in compositions of members of the ferrotorryweiserite (Ftyw) – torryweiserite (Tyw) series at River Ko, Eastern Sayans, Russia (this study), from the Marathon deposit, Coldwell complex, Ontario, Canada (this study and a mean composition in McDonald *et al*., 2021 [3], the Tulameen Alaskan-type complex, British Columbia, Canada after Aubut, 1979 [13], the Yubdo placer deposit in Ethiopia after Evstigneeva, 1992 [14], and the Miass placer zone, southern Urals, Russia, after Barkov *et al*., 2018 [15].

3.3. Crystallography and results of synchrotron micro-Laue diffraction study

A single crystal study could not be conducted because of the insuffient grain-sizes. Thus, we have performed synchrotron X-ray scans of ferrotorryweiserite grains with Laue microdiffraction measurements at beam line 12.3.2 of the Advanced Light Source (ALS). The Laue diffraction patterns were collected using a PILATUS 1M area detector in reflection geometry. The patterns were indexed and analyzed using XMAS v.6 (Tamura, 2014) [12]. Monochromator energy scans were performed to determine the unit-cell parameters of ferrotorryweiserite. These results indicate that crystal system is trigonal, and the probable space group, $R\bar{3}m$ (#166), is inferred by analogy with the Ni-dominant analogue, i.e. torryweiserite from the Marathon deposit, Coldwell complex, Ontario, Canada [2, 3]. The obtained unit cell parameters are: a = 7.069 (2) Å, c = 34.286 (11) Å, V = 1484 (1) Å^3, and Z = 3.

The X-ray powder-diffraction data obtained for ferrotorryweiserite using synchrotron micro-Laue diffraction [12] are listed in Table 3, together with those observed for torryweiserite (IMA2020-048) from the Marathon deposit, Coldwell complex, Ontario, Canada [3]. Comparison of characteristics of ferrotorryweiserite with those of related species is given in Table 4. On the basis of these results, we infer that ferrotorryweiserite is isostructural with torryweiserite. By analogy with the structural motif and assignments worked out for torryweiserite by McDonald *et al.*, 2021 [3], it is thus composed of three distinct layers of polyhedra that are stacked along [001]. The first is a layer of $Rh1S_6$ octahedra sharing edges; it has octahedral voids, such as are found in dioctahedral micas. The second is a mixed layer composed of $Rh2S_6$ octahedra, $Fe1S_4$ and $Fe2S_4$ tetrahedra arranged in a pinwheel fashion, with $Rh2S_6$ at the center. The third layer consists of a double sheet of $Fe3S_4$ tetrahedra that share edges along [001] to form six-membered $Fe3S_4$ rings. The structure is thus related to that of synthetic $Cu_4Sn_7S_{16}$ [16]. It is described in detail in the article on torryweiserite [3].

Table 4. X-ray powder diffraction data (d in Å) for ferrotorryweiserite

				Ferrotorryweiserite					Torryweiserite			
h	***k***	***i***	***l***	d_{obs} **(Å)**	d_{calc} **(Å)**	I_{meas}	I_{calc}		d_{obs} **(Å)**	d_{calc} **(Å)**	I_{obs}	I_{calc}
0	0	0	3	11.4287	11.4287	10.0	1.0					
1	**0**	**-1**	**2**	**5.7650**	5.7653	**38.6**	9.7			5.758		6
0	**0**	**0**	**6**	**5.7143**	5.7143	**60.8**	10.9			5.712		12
1	1	-2	0	3.5343	3.5345	10.7	13.8		3.566	3.530	17	14
2	-1	-1	3	3.3765	3.3767	20.2	0.5					
2	**0**	**-2**	**1**	**3.0486**	3.0488	**39.4**	38.1		**3.080**	**3.045**	**33**	**37**
1	**1**	**-2**	**6**	3.0058	3.0060	**36.5**	100.0		**3.029**	**3.003**	**58**	**100**
1	0	-1	10	2.9914	2.9914	21.3	51.2			2.990		51
2	**0**	**-2**	**5**	**2.7950**	2.7951	**100**	58.5		**2.817**	**2.792**	**23**	**60**
2	**0**	**-2**	**7**	**2.5956**	2.5958	**37.8**	2.6					
2	-1	-1	9	2.5910	2.5911	6.3	1.4					
2	0	-2	8		2.4909		21.5		2.508	2.488	17	14
3	-1	-2	1	2.2929	2.3086	12.3	3.0					
0	0	0	15	2.2857	2.2857	8.6	2.9			2.282		5
2	0	-2	10	2.2833	2.2834	22.4	2.8					
1	0	-1	14	2.2738	2.2738	8.3	0.2					
2	0	-2	11	2.1839	2.1839	15.6	25.7		2.199	2.182	21	23
3	-1	-2	7	2.0920	2.0922	12.6	0.7					
3	0	-3	3	2.0087	2.0089	9.8	0.2					
3	0	-3	6	1.9217	1.9218	6.2	28.3		**1.9329**	**1.9195**	**30**	**25**
0	0	0	18	1.9048	1.9048	6.2	0.0			1.9039		7
2	**2**	**-4**	**0**	**1.7671**	1.7673	**44.4**	90.0		**1.7797**	**1.7650**	**100**	**77**
2	0	-2	16	1.7554	1.7555	9.1	82.8			**1.7542**		**70**
3	-1	-2	13	1.7393	1.7394	7.2	1.5					
4	-2	-2	6	1.6882	1.6884	7.5	2.4					
2	0	-2	17	1.6841	1.6841	28.3	10.1		1.6929	1.6830	9	9
3	-1	-2	14	1.6818	1.6819	20.3	1.8					
4	0	-4	1		1.5290		5.0		1.5380	1.5270	12	5
0	2	-2	19		1.5545		1.3					

1	**3**	**-4**	**10**	**1.5243**	**1.5216**	**8.9**	**13.2**			**1.5199**		**12**
3	**0**	**-3**	**15**		1.5223		2.2					
4	**-2**	**-2**	**12**	**1.5029**	1.5067	**35.3**	0.1					
4	0	-4	5	1.4936	1.4937	11.3	8.1			1.4920		10
3	1	-4	11		1.4910		2.7					
4	-2	-2	15	1.3980	1.3981	8.0	3.9					
2	3	-5	5		1.3750		1.5					
4	0	-4	11		1.3738		5.1			1.3723		5
2	0	-2	23	1.3402	1.3402	8.3	0.2					
4	1	-5	6		1.3008		4.8		**1.3072**	**1.2992**	**23**	**18**
3	2	-5	10		1.2997		1.7					
4	-2	-2	18	1.2955	1.2926	7.4	3.8					
4	0	-4	16		1.2454		23.8		**1.2512**	**1.2442**	**49**	**21**
4	0	-4	17	1.2191	1.2192	5.6	3.3					
2	2	-4	21		1.1992		7.5			1.1982		12
1	1	-2	27		1.1951		2.2					
4	2	-6	1		1.1563		1.3					
3	3	-6	6		1.1539		1.5		1.1598	1.1517	17	17
1	3	-4	22		1.1481		3.50					

Note: Only reflections with $I \geq 5$ are listed.

Table 5. Comparison of characteristics of ferrotorryweiserite with those of related species

#	Species	Type locality	Ideal formula	Unit cell parameters	Reference
1	Ferrotorryweiserite*	River Ko deposit, Sisim placer zone, southwestern Eastern Sayans, Russia	$Rh_5Fe_{10}S_{16}$	*a* = 7.069 (2) Å *c* = 34.286 (11) Å *V* = 1484 (1) Å^3 and *Z* = 3	(This study)
2	Torryweiserite	Marathon deposit, Coldwell complex, Ontario, Canada	$Rh_5Ni_{10}S_{16}$	*a* = 7.060 (1) Å, *c* = 34.271 (7) Å, *V* = 1479.3 (1) Å^3, and *Z* = 3	McDonald *et al.* 2021 [3]
3	Tamuraite	River Ko deposit	$Ir_5Fe_{10}S_{16}$	*a* = 7.073 (1) Å *c* = 34.277 (8) Å	Barkov *et al.,* 2021 [5]
3	Kuvaevite	River Ko deposit	$Ir_5Ni_{10}S_{16}$	*a* = 7.079 (5) Å *c* = 34.344 (12) Å and Z = 3	IMA2020-043 [6]

Note: Unit-cell parameters refined from 177 reflections indexed for the ferrotorryweiserite grain $(Rh_{3.46}Ir_{1.43}Pt_{0.08}Ru_{0.02}Os_{0.01})_{\Sigma 5.00}(Fe_{4.38}Ni_{3.80}Cu_{1.76}Co_{0.02})_{\Sigma 9.96}S_{16.04}$ studied by synchrotron micro-Laue diffraction. The space group $R\bar{3}m$ (#166) is inferred for these compounds by analogy with torryweiserite [3].

3.4. Name and type material

The name ferrotorryweiserite reflects its iron-dominant composition and indicates that it represents the Fe-dominant analogue of torryweiserite.

The holotype specimen of ferrotorryweiserite is deposited (catalog number: III-102/3) at the Central Siberian Geological Museum, Sobolev Institute of Geology and Mineralogy, Akademik Koptyug Avenue, no. 3, 630090 Novosibirsk, Russia.

Discussion

4.1. Relation to other species

As noted, ferrotorryweiserite $Rh_5Fe_{10}S_{16}$ is isostructural with torryweiserite $Rh_5Ni_{10}S_{16}$ [3] found at the type locality, i.e. the Marathon deposit, Coldwell complex, Ontario, Canada. Ferrotorryweiserite is the Fe-dominant analogue of torryweiserite, and forms a well-defined series of solid solution with torryweiserite (Figure 2a, b; Tables 2, 3). Therefore, ferrotorryweiserite belongs to the torryweiserite family of ternary sulfide minerals crystallized in space group $R\bar{3}m$ (#166), which also includes tamuraite $Ir_5Fe_{10}S_{16}$ [5] and kuvaevite $Ir_5Ni_{10}S_{16}$ [6] (Table 5).

Ferrotorryweiserite is distinct from oberthürite ($Rh_3Ni_{32}S_{32}$), both compositionally and structurally; oberthürite is a member of the pentlandite group (with *a* = 10.066(5) Å) from the Marathon deposit, Coldwell complex, Ontario, Canada [3]. Ferrotorryweiserite also differs from ferhodsite [$(Fe,Rh,Ir,Ni,Cu,Co,Pt)_{9-x}S_8$] described at Nizhniy Tagil, Urals. The latter has a tetragonal unit-cell (*P*42/*n* or *P*4/*nmm*) with parameters *a* = 10.009(5) and *c* = 9.840(8) Å [17].

4.2. Genetic implications and the ferrotorryweiserite – weiserite series

The inferred terrane affinities and mineral associations point that the placer PGM grains with inclusions of the ferrotorryweiserite-torryweiserite solid solution are related to zones of chromitite within ultramafic units of the Lysanskiy layered complex of dunite–peridotite–gabbro. As noted, this complex is the likely primary source for the PGM-bearing placers for the entire Sisim placer zone. The direct intergrowths of PGM with a REE mineral, documented at Sisim [9], resemble examples of atypical mineralization reported from the Oktyabrsky deposit, Norilsk complex, Russia 17].

Members of the ferrotorryweiserite-torryweiserite series associated with the tamuraite-kuvaevite solid-solution likely formed at an advanced stage of crystallization as a result of buildup in sulfur in droplets of incompatible residual melt enriched in Ni, Fe, Cu, Rh and lithophile elements during the formation of the alloys in lode zones of chromitites in the Lysanskiy layered complex, Eastern Sayans.

The Fe-for-Ni substitution is determinative for members of the inferred ferrotorryweiserite – torryweiserite series (Figure 2a, b), as is indicated by the quoted data from the River Ko placer, Eastern Sayans, Russia (this study), the Marathon deposit, Coldwell complex, Ontario, Canada [3], the Tulameen Alaskan-type complex, British Columbia, Canada [13], the Yubdo placer deposit in Ethiopia [14, 19], and the Miass placer zone, southern Urals, Russia [15].

A plot of Fe vs. Ni (Figure 2a) shows a negative correlation (R = –0.73), calculated for Fe vs. Ni on the basis of a total of 39 data-points available for members of the series, which contain substantial Cu. The Rh vs. Ir correlation is inverse (R = –0.97 for n=39: Figure 2b). Note that correlations of Fe vs. Rh, Fe vs. Ir, Ni vs. Rh, and Ni vs. Ir all are statistically insignificant. Thus, the observed substitutions of Fe vs. Ni and Rh vs. Ir operate independently in the structure of members of this series, consistent with the idea that these ions largely occupy different crystallographic sites. This inference is corroborated by crystal-chemical considerations reported for the type specimen of torryweiserite from the Marathon deposit, Coldwell complex, Ontario, Canada [3].

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