### ORIGINAL PAPER

# Nickelpicromerite, K<sub>2</sub>Ni(SO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O, a new picromerite-group mineral from Slyudorudnik, South Urals, Russia

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Abstract A new picromerite-group mineral, nickelpicromerite,  $K_2Ni(SO_4)_2 \cdot 6H_2O$  (IMA 2012–053), was found at the Vein #169 of the Ufaley quartz deposit, near the town of Slyudorudnik, Kyshtym District, Chelyabinsk area, South Urals, Russia. It is a supergene mineral that occurs, with gyp-sum and goethite, in the fractures of slightly weathered actinolite-talc schist containing partially vermiculitized biotite and partially altered sulfides: pyrrhotite, pentlandite, millerite, pyrite and marcasite. Nickelpicromerite forms equant to short prismatic or tabular crystals up to 0.07 mm in size and anhedral grains up to 0.5 mm across, their clusters or crusts up to 1 mm. Nickelpicromerite is light greenish blue. Lustre is vitreous.

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Fersman Mineralogical Museum of Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia Mohs hardness is  $2-2\frac{1}{2}$ . Cleavage is distinct, parallel to  $\{10-2\}$ .  $D_{\text{meas}}$  is 2.20(2),  $D_{\text{calc}}$  is 2.22 g cm<sup>-3</sup>. Nickelpicromerite is optically biaxial (+),  $\alpha = 1.486(2)$ ,  $\beta = 1.489(2), \gamma = 1.494(2), 2V_{\text{meas}} = 75(10)^{\circ}, 2V_{\text{calc}} = 76^{\circ}$ . The chemical composition (wt.%, electron-microprobe data) is: K<sub>2</sub>O 20.93, MgO 0.38, FeO 0.07, NiO 16.76, SO<sub>3</sub> 37.20, H<sub>2</sub>O (calc.) 24.66, total 100.00. The empirical formula, calculated based on 14 O, is: K<sub>1.93</sub>Mg<sub>0.04</sub>Ni<sub>0.98</sub>S<sub>2.02</sub>O<sub>8.05</sub>(H<sub>2</sub>O)<sub>5.95</sub>. Nickelpicromerite is monoclinic,  $P2_1/c$ , a=6.1310(7), b=12.1863(14), c=9.0076(10) Å,  $\beta=105.045(2)^{\circ}$ , V=649.9(1)Å<sup>3</sup>, Z=2. Eight strongest reflections of the powder XRD pattern are [d, Å-I(hkl)]: 5.386–34(110); 4.312–46(002); 4.240– 33(120); 4.085-100(012, 10-2); 3.685-85(031), 3.041-45(040, 112), 2.808-31(013, 20-2, 122), 2.368-34(13-3, 21-3, 033). Nickelpicromerite (single-crystal X-ray data, R=0.028) is isostructural to other picromerite-group minerals and synthetic Tutton's salts. Its crystal structure consists of  $[Ni(H_2O)_6]^{2+}$  octahedra linked to  $(SO_4)^{2-}$  tetrahedra via hydrogen bonds. K<sup>+</sup> cations are coordinated by eight anions. Nickelpicromerite is the product of alteration of primary sulfide minerals and the reaction of the acid Ni-sulfate solutions with biotite.

# Introduction

The structural and chemical diversity of the sulfate minerals continues to be in the focus of many mineralogical and crystal-chemical studies (Plášil et al. 2013a, b, c; Pekov et al. 2013, 2014a, b; Chukanov et al. 2013; Galli et al. 2013; Kampf et al. 2013; Demartin et al. 2013; Kasatkin et al. 2013; Murashko et al. 2013, etc.). The interest to sulfates was renewed after the discovery of hydrous metal sulfates on Mars that led to the increase in the number of publications devoted to their crystal chemistry and thermodynamic properties (for the relevant recent papers

Table 1         Comparative	e data for picromerite-grou	ip minerals				
Mineral formula	Nickelpicromerite K_Ni(SOL), 6H,O	Picromerite K <sub>2</sub> Ma(SO <sub>2</sub> )2.6H <sub>2</sub> O	Cyanochroite K <sub>2</sub> Cu(SO.), 6H <sub>2</sub> O	Nickelboussingaultite	Boussingaultite	Mohrite
Crystal system Space group	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$
Unit cell data						
$a, \mathrm{\AA}$	6.131	6.113	6.149	6.244	6.202	6.24
$b, \mathrm{\AA}$	12.186	12.212	12.13	12.469	12.580	12.65
$c, \mathrm{\AA}$	9.008	9.072	9.066	9.195	9.316	9.32
β, °	105.05	104.83	104.4	106.98	107.09	106.8
$V, Å^3$	650	655	655	685	695	704
Ζ	2	2	2	2	2	2
Optical data						
α	1.486	1.461	1.484 - 1.485	1.490	1.470	1.480 - 1.486
β	1.489	1.463	1.486 - 1.488	1.494	1.472	n.d.
λ	1.494	1.476	1.502	1.501	1.479	1.486 - 1.497
optical sign, 2 V	+75°	+48°	+46°	(+) 2 V not determined	+51°	+75°
Density, g cm <sup><math>-3</math></sup>	2.20 meas.	2.03 meas.	2.22 meas.	1.85 calc.	1.72 meas.	1.80–1.86 meas.
	2.22 calc.	2.03 calc.	2.23 calc.		1.72 calc.	1.80–1.87 calc.
References	This work	Kannan and Viswamitra (1965); Anthony et al. (2003)	Robinson and Kennard (1972); Anthony et al. (2003)	Yakhontova et al. (1976); Tahirov et al. (1994)	Maslen et al. (1988); Anthony et al. (2003)	Garavelli (1964); Montgomery et al. (1967)
Unit-cell data are given $c > a$ )	for synthetic analogues of	end-members of all listed miner	als except nickelpicromerite. C	rystal data for all minerals are giv	ven for the setting corresponding	to space group $P2_1/c$ ( $b >$

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Fig. 1 Crystal clusters of nickelpicromerite. SEM (SE) images

see: Chou et al. 2013; Szynkiewicz et al. 2014; Wang and Zhou 2014, etc.).

In this paper, we report on the occurrence, composition, structure and properties of nickelpicromerite (Cyrillic: никельпикромерит), ideally  $K_2Ni(SO_4)_2 \cdot 6H_2O$ , a new mineral of the picromerite group that currently includes five isotypic sulfate minerals with the general formula  $A^+_2M^{2+}(SO_4)_2 \cdot 6H_2O$ , where A=K or NH<sub>4</sub> and M=Mg, Fe, Ni or Cu (Table 1). The synthetic picromerite-type  $K_2Ni(SO_4)_2 \cdot 6H_2O$  is well-known (Bosi et al. 2009). Its natural analogue was discovered by us and briefly described previously as "a new hydrous sulfate of potassium and nickel" (Belogub et al. 2009).

Both the new mineral and its name have been approved by the IMA CNMNC, No. 2012–053. The cotype specimens are deposited in the collection of the Natural Scientific Museum of the Ilmen State Reserve, Miass (catalogue number 17301), and in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow (catalogue number 93776).

#### Occurrence and general appearance

Nickelpicromerite was found at the Vein #169 of the Ufaley quartz deposit, near the town of Slyudorudnik, Kyshtym District, Chelyabinsk Oblast, South Urals, Russia (55°40'12" N 60°21'17"E). The new mineral occurs together with gypsum and goethite in fractures of slightly weathered actinolitetalc schist containing partially altered (vermiculitized) biotite and sulfides (pyrrhotite, pentlandite, millerite, pyrite and marcasite) and, rarely, unaltered chromite. Nickelpicromerite forms equant to short prismatic or tabular crystals up to 0.07 mm in size and anhedral grains up to 0.5 mm (typically less than 0.1 mm) across, their clusters (Fig. 1) or crusts up to 1 mm. By analogy with picromerite (Palache et al. 1951), the following major crystal forms have been assumed: {111}, {011}, {010} and {10-2}; the forms {100} and {001} are subordinate (Fig. 2).



Fig. 2 Idealised crystal habit of nickelpicromerite

## Physical properties and optical data

Nickelpicromerite is transparent, light greenish blue (light turquoise-coloured), with white streak. The lustre is vitreous. The mineral does not exhibit fluorescence either in UV or in cathode rays. Its Mohs' hardness is  $2-2\frac{1}{2}$ . Nickelpicromerite is brittle. The cleavage is distinct, probably on {10–2} (by analogy with picromerite). The fracture is stepped. Density measured by flotation in CHBr<sub>3</sub> + CH<sub>3</sub>OH is 2.20(2) g cm<sup>-3</sup>; calculated density is 2.222 g/cm<sup>3</sup> (using the empirical formula). Nickelpicromerite is optically biaxial (+),  $\alpha = 1.486(2)$ ,  $\beta = 1.489(2)$ ,  $\gamma = 1.494(2)$ ,  $2V_{meas} = 75(10)^{\circ}$ ,  $2V_{calc} = 76^{\circ}$ .

#### Infrared spectroscopy

Nickelpicromerite powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm<sup>-1</sup>. Accumulation of 16 scans was done. A pellet of pure KBr was used as a reference.

Absorption bands in the IR spectrum of nickelpicromerite (Fig. 3) and their assignments are (cm<sup>-1</sup>; s – strong band, w – weak band, sh – shoulder): 3365sh, 3290sh, 3237 s, 3180sh (O-H stretching vibrations); 2208w (overtone or combination mode of asymmetric S-O stretching vibrations); 1622w, 1560w (H-O-H bending vibrations); 1142s, 1100s (asymmetric S-O stretching vibrations); 985 (symmetric S-O stretching vibrations); 894w, 850w, 763 (librational modes of H<sub>2</sub>O molecules); 632, 618, 581w (O-S-O bending vibrations); 530w, 461w, 445w, 416w, 366w (lattice modes involving librational

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vibrations of  $SO_4^{2-}$  anions, Ni-O stretching vibrations, and/or acoustic modes).

The relatively low intensity of the symmetric S-O stretching band at 985 cm<sup>-1</sup> points to a weak distortion of the SO<sub>4</sub> tetrahedra. This band corresponds to a non-degenerate mode and is not split, which supports the fact that the structure of nickelpicromerite contains one symmetrically unique of SO<sub>4</sub><sup>2-</sup> anions only. The splitting of the non-degenerate H-O-H bending vibration band indicates the presence of non-equivalent H<sub>2</sub>O molecules. Bands that could be assigned to NH<sub>4</sub><sup>+</sup> cations as well as to CO<sub>3</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> anions in the range 1300–1500 cm<sup>-1</sup> are absent.

The IR spectra of nickelpicromerite and picromerite are very similar. The strongest bands in the picromerite spectrum are at 3280, 1652, 1147, 1100, 985, 750, 630 and 614 cm<sup>-1</sup> (Chukanov 2014).

The IR spectrum of the synthetic analogue of nickelpicromerite has been published in numerous papers, but most available literature data are incomplete and partly erroneous. In (Rocchiccioli 1964) only a schematic presentation of the IR spectrum of  $K_2Ni(SO_4)_2 \cdot 6H_2O$  is given. In the wavenumber range from 970 to 1030 cm-1 corresponding to the non-degenerate S–O stretching mode, two bands are indicated, which is impossible taking into account the presence of only one kind of SO<sub>4</sub> groups in the structure. As one can see from Fig. 3, IR spectrum of natural nickelpicromerite contains in this range only one absorption band with the maximum at 985 cm-1. Publication (Polovynko et al. 2009) contains IR spectra of a poor quality and a number of serious mistakes. In particular, the band in the range from 762 to 767 cm<sup>-1</sup> is

Fig. 3 Infrared-absorption spectrum of nickelpicromerite



Table 2	Powder X-ray
diffractio	n data for
nickelpic	romerite

I <sub>obs</sub>	$d_{obs}, Å$	I <sub>calc</sub>	d <sub>calc</sub> , Å*	h k l
27	6.123	21	6.093	020
34	5.386	7	5.326	110
21	5.110	8	5.104	11–1
46	4.312	28	4.349	002
33	4.240	15	4.246	120
100	4.085	4, 100	4.096, 4.041	012, 10–2
85	3.685	68	3.681	031
14	3.560	4, 5	3.563, 3.540	121, 022
20	3.317	6,14	3.350, 3.292	130, 13–1
15	3.136	17	3.138	102
45	3.041	19, 13	3.047, 3.039	040, 112
29	2.984	2, 1, 37	2.982, 2.969, 2.963	131, 032, 21–1
31	2.808	8, 10, 15	2.821, 2.810, 2.790	013, 20–2, 122
24	2.721	4, 9, 4	2.738, 2.731, 2.678	21-2, 22-1, 14-1
3	2.634	3	2.634	12–3
5	2.541	2, 1	2.552, 2.546	22–2, 211
7	2.497	2, 4, 5	2.503, 2.495, 2.483	141, 042, 132
34	2.368	27, 1, 1	2.371, 2.362, 2.360	13-3, 21-3, 033
11	2.248	3, 2, 1	2.254, 2.239, 2.238	150, 22–3, 10–4
22	2.185	3, 2, 14, 2	2.196, 2.192, 2.186, 2.175	202, 231, 142, 004
15	2.139	2, 2, 9	2.141, 2.131, 2.123	014, 151, 240
18	2.057	7.9	2.066, 2.048	24–2.024
13	1.979	14	1.974	300
11	1.922	3.1.2	1.925, 1.921, 1.918	152, 160, 22–4
6	1.904	1	1.903	32–2
15	1.866	3.4	1.871 1.866	15-3,053
5	1.853	5	1.852	31-3
2	1.842	1.1	1 843 1 840	161.062
13	1.823	5 6	1 825 1 815	33-1 16-2
4	1 799	3	1 797	33-2
10	1.772	2 5	1 775 1 770	330_044
12	1.714	5,1,1	1 722 1 713 1 713	015 134 25-3
12	1.679	3, 1, 1	1 680 1 675 1 674 1 673	233 260 34_2 025
2	1.645	1 1	1 646 1 644	255, 200, 54 2, 025
2 4	1.649	1, 1	1 623 1 618	054 171
7 2	1.607	1, 5	1 605	144
2	1.584	1	1 587	322
2	1.569	2 1 1	1.567	322 22 5 204 22 4
0 2	1.509	5, 1, 1	1.575, 1.509, 1.500	23-3, 204, 33-4 40, 2
5	1.528	4	1.527	40-2
9	1.309	5,2	1.512, 1.504	27-1, 10-4
3	1.490	1, 2	1.493, 1.491	073, 262
4	1.480	3	1.483	34-4
4	1.452	1, 1	1.404, 1.447	313, 2/1
4	1.431	1, 2	1.432, 1.429	20-4, 43-1
4	1.399	2, 1	1.403, 1.398	173, 25-5
3	1.364	1, 1	1.366, 1.358	263, 361
3	1.318	1, 1, 1	1.319, 1.319, 1.316	254, 27–4, 19–1
3	1.299	1, 1, 1	1.300, 1.295, 1.294	41-5, 412, 45-2

\*Calculated from the unit-cell parameters obtained from single-crystal data 
 Table 3
 Crystallographic data

 and refinement parameters for
 nickelpicromerite

Crystal data	
Temperature	293 K
Radiation, wavelength	Mo $K_{\alpha}$ , 0.71073 Å
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit-cell dimensions $a, b, c$ (Å), $\beta$ (°)	6.1310(7), 12.1863(14), 9.0076(10), 105.045(2)
Unit-cell volume (Å <sup>3</sup> )	649.9(1)
Ζ	2
Calculated density (g/cm <sup>3</sup> )	2.234
Absorption coefficient (mm <sup>-1</sup> )	2.522
Crystal size (mm <sup>3</sup> )	0.22×0.16×0.12
Data collection	
θ range	$2.88 - 29.28^{\circ}$
h, k, l ranges	$-8 \rightarrow 8, -16 \rightarrow 16, -12 \rightarrow 12$
Total reflections collected	8036
Unique reflections $(R_{int})$	1775 (0.024)
Unique reflections $F > 4\sigma(F)$	1585
Structure refinement	
Refinement method	Full-matrix least-squares on $F^2$
Weighting coefficients a, b	0.0497, 0.5367
Extinction coefficient	0.0000(14)
Data/restraints/parameters	1775/6/108
$R_1 [F > 4\sigma(F)], wR_2 [F > 4\sigma(F)],$	0.028, 0.084
$R_1$ all, $wR_2$ all	0.032, 0.087
Goodness-of-fit on $F^2$	1.076
Largest diff. peak and hole, e $Å^{-3}$	0.49, -0.83

erroneously assigned to OH-stretching vibrations. Some expressions like "combination mode of OH-stretching and

hydrogen bond OH" used in this publication are absolutely unclear.

 Table 4
 Coordinates and displacement parameters (Å<sup>2</sup>) of atoms in nickelpicromerite

Atom	x/a	y/b	z/c	Uiso/Ueq	Atom	$U_{11}$	<i>U</i> <sub>22</sub>	U <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	$U_{12}$
Ni	0	0	0	0.0179(1)	Ni	0.0187(2)	0.0184(2)	0.0164(2)	-0.0010(1)	0.0040(2)	0.0001(1)
S	0.27354(9)	0.63533(4)	0.08855(6)	0.0175(1)	S	0.0184(2)	0.0183(3)	0.0154(2)	0.0025(2)	0.0039(2)	0.0019(2)
Κ	0.3425(1)	0.34587(5)	0.13373(7)	0.0304(2)	Κ	0.0302(3)	0.0310(3)	0.0320(3)	-0.0024(2)	0.0117(2)	-0.0004(2)
$O_w 1$	-0.3010(3)	0.06701(13)	0.0006(2)	0.0221(3)	$O_w 1$	0.0206(7)	0.0200(7)	0.0272(8)	0.0017(6)	0.0091(6)	0.0030(6)
O <sub>w</sub> 2	0.1632(3)	0.11059(14)	0.16755(19)	0.0227(3)	O <sub>w</sub> 2	0.0213(8)	0.0249(8)	0.0202(8)	-0.0066(6)	0.0025(6)	-0.0004(6)
O <sub>w</sub> 3	-0.0349(3)	-0.11251(13)	0.16655(18)	0.0215(3)	O <sub>w</sub> 3	0.0259(8)	0.0208(8)	0.0179(7)	0.0016(6)	0.0058(6)	0.0002(6)
O4	0.3809(3)	0.56177(14)	0.21601(18)	0.0239(4)	04	0.0259(8)	0.0257(8)	0.0198(8)	0.0081(6)	0.0054(6)	0.0052(6)
05	0.0532(3)	0.67388(14)	0.1063(2)	0.0272(4)	05	0.0209(8)	0.0245(8)	0.0377(10)	0.0038(7)	0.0103(7)	0.0044(7)
06	0.4247(3)	0.72965(15)	0.0908(2)	0.0330(4)	06	0.0255(9)	0.0237(9)	0.0492(12)	0.0112(8)	0.0087(8)	-0.0021(7)
07	0.2439(4)	0.57532(19)	-0.0564(2)	0.0398(5)	07	0.045(2)	0.053(1)	0.0183(8)	-0.0086(8)	0.0016(8)	0.010(1)
H1	0.067(6)	-0.105(4)	0.264(3)	0.080*							
H2	0.307(4)	0.083(4)	0.216(5)	0.080*							
H3	-0.331(8)	0.1414(13)	-0.024(5)	0.080*							
H4	-0.010(8)	-0.1830(18)	0.131(5)	0.080*							
Н5	-0.328(8)	0.056(4)	0.097(3)	0.080*							
H6	0.093(8)	0.128(4)	0.246(4)	0.080*							

\*Fixed during refinement

Nickelpicromerite	$K_2Ni(SO_4)_2$ •6	H <sub>2</sub> O, new pic	romerite-group	mineral
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Table 5         Selected           interatomic distances (Å)	Ni-O <sub>w</sub> 1	2.019(2) 2x	K-04	2.727(2)		
and hydrogen bonding	Ni-O <sub>w</sub> 2	2.076(2) 2x	K-O5	2.810(2)		
scheme for	Ni-O <sub>w</sub> 3	2.084(2) 2x	K-06	2.891(2)		
nickelpicromerite	<ni-o<sub>w&gt;</ni-o<sub>	2.060	K-06	2.911(2)		
			K-07	2.959(2)		
	S-07	1.466(2)	K-O <sub>w</sub> 3	2.969(2)		
	S-04	1.471(2)	K-O <sub>w</sub> 2	3.114(2)		
	S-O6	1.474(2)	K-07	3.253(2)		
	S-O5	1.478(2)	<k-o></k-o>	2.954		
	<s-o></s-o>	1.472				
	D	d(D-H)	d(HA)	<dha< td=""><td>d(DA)</td><td>А</td></dha<>	d(DA)	А
	O <sub>w</sub> 3	0.943	1.733	173.61	2.672	07
	O <sub>w</sub> 2	0.936	1.872	163.61	2.783	04
	O <sub>w</sub> 1	0.940	1.726	170.79	2.659	O6
	O <sub>w</sub> 3	0.941	1.814	167.81	2.741	05
	O <sub>w</sub> 1	0.938	1.795	169.26	2.722	O4
D donor 1 accontor	O <sub>w</sub> 2	0.942	1.873	174.77	2.812	05
D donor, A acceptor						

A representative collection of IR spectra of Tutton compounds, M'2 M"(XO4)2·6H2O (M'=K, NH4+; M"=Mg, Co, Ni, Cu, Zn; X=S, Se), is published by Marinova et al. (2015) and discussed in the regions of v3 and v1 of SO<sub>4</sub><sup>2–</sup> guest ions, v4 of NH<sup>4+</sup> guest ions and water librations. IR spectrum of synthetic K<sub>2</sub>Ni(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O given in this paper is practically identical to the spectrum of nickelpicromerite.

# Chemical data

The chemical composition of nickelpicromerite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Local Methods of Matter Investigations, Faculty of Geology, Moscow State University). The operating voltage was 15 kV, the beam current was 20 nA, and the electron beam was rastered over  $10 \times 10 \ \mu m^2$  to minimise sample damage. The following standards were used: orthoclase (K), olivine (Mg), CuFeS<sub>2</sub> (Fe), Ni (Ni) and SrSO<sub>4</sub> (S). H<sub>2</sub>O was not measured because of the scarcity of pure material, but its presence is clearly confirmed by the crystal structure data and IR spectrum.

The average of five analyses provided the following data (wt. %, with ranges in parentheses):  $K_2O$  20.93 (20.0–22.1), MgO 0.38 (0.0–1.0), FeO 0.07 (0.0–0.2), NiO 16.76 (15.6–17.4), SO<sub>3</sub> 37.20 (35.9–38.3), H<sub>2</sub>O (calc.) 24.66, total 100.00. The H<sub>2</sub>O content was calculated by difference; the correctness of the value is clearly confirmed by the crystal structure

Fig. 4 The crystal structure of nickelpicromerite projected along the *c* axis. Ni-centered octahedra and SO<sub>4</sub> tetrahedra are shown. H-bonds are shown as *thin dark* grey lines. The unit cell is outlined



refinement. Contents of other elements with the atomic numbers higher than carbon are below detection limits.

The empirical formula, calculated on the basis of 14 O apfu, is:  $K_{1.93}Mg_{0.04}Ni_{0.98}S_{2.02}O_{8.05}(H_2O)_{5.95}$ . The simplified formula is  $K_2Ni(SO_4)_2 \cdot 6H_2O$ , which requires  $K_2O$  21.55, NiO 17.09, SO<sub>3</sub> 36.63, H<sub>2</sub>O 24.73, total 100.00 wt.%.

The Gladstone-Dale compatibility index  $[1 - (K_p/K_c)]$ (Mandarino 1981) value is 0.004 (superior).

Nickelpicromerite easily dissolves in water at room temperature. Its solution is weakly acidic (pH =5–5.5) and shows a distinct reaction with  $BaCl_2$  with the formation of a white  $BaSO_4$  precipitate.

#### X-ray crystallography and crystal structure

Powder X-ray diffraction data for nickelpicromerite (Table 2) were obtained with a STOE IPDS II singlecrystal diffractometer equipped with an image plate detector (MoK $\alpha$  radiation; the sample-to-detector distance was set at 200 mm) using the Gandolfi method. The unit-cell parameters calculated from the powder data using STOE software are: a=6.13(1), b=12.22(1), c=8.98(2) Å,  $\beta=$  105.1(1)°, V=650(2) Å<sup>3</sup>.

Single-crystal X-ray diffraction studies of nickelpicromerite were carried out using a Bruker Smart APEX II CCD diffractometer equipped with a CCD detector. Systematic absences were consistent with the space group  $P2_1/c$  reported for the synthetic analogue (Bosi et al. 2009; note that we use standard space-group setting instead of the non-standard  $P2_1/a$  used in the previous works). We not that the unit-cell parameters of nickelpicromerite (a=6.1310(7), b=12.1863(14), c=9.0076(10) Å,  $\beta=$  $105.045(2)^{\circ}$  are almost identical to those of its synthetic counterpart (a=6.1368(5), b=12.1904(8), c=9.0049(4) Å,  $\beta = 105.047(5)^{\circ}$ ). The structure was solved by direct methods and refined with the use of the SHELX software package (Sheldrick 2008) to R=0.028 for 1585 unique reflections with  $F > 4\sigma(F)$ . The positions of the H atoms have been deduced from the difference Fourier electron-density maps; in the final refinement the D-H distances (D=donor) were restrained at 0.95(1) Å. Crystal data, data collection information and structure refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4 and selected interatomic distances, including the hydrogen bonding scheme, in Table 5.

A broad absorption band in the range from 3000 to  $3500 \text{ cm}^{-1}$  can be put into correspondence with donor-acceptor distances D..A for hydrogen bonds. Indeed, the following empirical correlation between O–H stretching frequencies in IR spectra of minerals and D..A distance

(from structural data) was established by Libowitzky (1999):

$$n(cm^{-1}) = 3592 - 304 \cdot 10^9 \cdot exp[-d(D..A)/0.1321]$$
(1)

According to this equation, the distances D..A ranging from 2.659 to 2.812 Å (Table 5) correspond to the wavenumbers from 3039 to  $3419 \text{ cm}^{-1}$ .

Ivanovski et al. (2008) describes IR reflectance spectrum of synthetic  $K_2Ni(SO_4)_2 \cdot 6H_2O$ . Six bands of O–H-stretching vibrations determined from the fit of the recorded spectrum with the polarization in the *ac* crystal plane are located at 3307.0, 3284.7, 3243.9, 3207.1, 3158.5 and 3073.8 cm<sup>-1</sup>. Despite direct comparison of reflectance and absorbance spectra is incorrect, this fact confirms the above conclusion that the value 3490 cm-1 obtained based on the Libowitzky correlation (1) for the D..A distance of 2.812 Å is overestimated.

It should be noted that substantial deviations from the correlation (1) are possible because O–H stretching frequencies depend not only on O···O distances, but also on the nature of cations coordinating O–H groups and H<sub>2</sub>O molecules, as well as on the angle O–H···O, and the influence of these factors becomes most evident in case of weak hydrogen bonds. The equation (1) predicts that maximum possible values of O–H stretching frequencies for minerals are 3592 and 3632 cm<sup>-1</sup> respectively. However, *e. g.* for magnesium serpentines, brucite and kaolinite observed frequencies are close to 3700 cm<sup>-1</sup>.

Nickelpicromerite (Fig. 4) is isostructural to other picromerite-group minerals (Table 1) and synthetic Tutton's salts with the general formula  $A_2^+ M^{2+}(SO_4)_2 \cdot 6H_2O$  (Kohler and Franke 1964; Prumova 1975; Pushcharovsky et al. 1998; Hawthorne et al. 2000; Bosi et al. 2009). It consists of the  $[Ni(H_2O)_6]^{2+}$  octahedral cations linked to  $(SO_4)^{2-}$  tetrahedra via complex system of hydrogen bonds. The K<sup>+</sup> cations are coordinated by eight anions. The NiO<sub>6</sub> octahedron in synthetic nickelpicromerite possesses almost the same geometry as that in its synthetic analogue reported by Bosi et al. (2009). The average <Ni-O> bond lengths are equal to 2.06 Å and are identical for natural and synthetic nickelpicromerite.

#### Discussion

Nickelpicromerite is a secondary, supergene mineral formed in the weathering zone of actinolite-talc schist with biotite and sulfides. In this rock, pentlandite, pyrrhotite and marcasite contain up to 37.9, 3.0 and 0.4 wt.% Ni, respectively. Sulfuric acid formed as a result of the oxidation of sulfides, mainly of a widespread pyrrhotite, reacts with biotite and transforms it into vermiculite, releasing K<sup>+</sup> cations into the environment. Therefore, sulfides are the obvious source of  $SO_4^{2-}$  and Ni<sup>2+</sup>, whereas biotite provides for the presence of  $K^+$  in secondary solutions. Iron oxidizes to  $Fe^{3+}$  and precipitates in the form of goethite. It is of interest that, in this assemblage, vermiculite contains up to 10 wt.% of NiO (our electron microprobe data). We assume that vermiculite could be an intermediate collector for Ni mobilized from sulfides (Ni probably substitutes for Mg and Fe in this phyllosilicate).

Nickelpicromerite is the ninth natural sulfate with speciesdefining nickel, after morenosite, retgersite (Palache et al. 1951), nickelhexahydrite (Oleinikov et al. 1965; Zubkova et al. 2008), nickelboussingaultite (Yakhontova et al. 1976; Tahirov et al. 1994), nickelblödite (Nickel and Bridge 1977), dwornikite (Milton et al. 1982), paraotwayite (Nickel and Graham 1987) and nickelzippeite (Burns et al. 2003). This list does not include members of the hydrotalcite supergroup (Mills et al. 2012) and of the chalcoalumite group (Martini 1980) belonging to SO<sub>4</sub>-bearing hydroxides. In most cases, the crystallization of nickel sulfates in nature happens from low-temperature Ni-bearing sulfate solutions formed as a result of alteration of primary Ni sulfides in the oxidation zone of ore deposits.

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