

Crystal chemistry of shuiskite and chromian pumpellyite-(Mg)

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Abstract: The crystal structures of two Cr-rich pumpellyite-group minerals, shuiskite with 22.6 wt% Cr₂O₃ from the Biserskoe deposit and chromian pumpellyite-(Mg) with 16.4 wt% Cr₂O₃ from the Glavnoe Saranovskoe deposit (both belong to the Saranovskaya group of chromite deposits, Middle Urals, Russia) were studied through single-crystal X-ray diffraction. The structures (space group *C2/m*) of shuiskite with *a* = 19.2156(7), *b* = 5.9779(2), *c* = 8.8268(3) Å, β = 97.785(3)° and chromian pumpellyite-(Mg) with *a* = 19.1776(8), *b* = 5.9537(3), *c* = 8.8282(4) Å, β = 97.668(4)° were refined to *R*₁ = 3.01 and 3.12%, respectively; the structure of shuiskite was determined for the first time. The formulae (*Z* = 4) obtained from the structural refinements and taking into account electron-microprobe data are: ^WCa_{2.00}^X(Mg_{0.46}Cr_{0.36}Al_{0.18})_{Σ1.00}^Y(Cr_{1.04}Al_{0.96})_{Σ2.00}^ZSi_{3.00}O_{10.54}OH_{3.46} for shuiskite and ^WCa_{2.00}^X(Mg_{0.50}Cr_{0.30}Al_{0.20})_{Σ1.00}^Y(Al_{1.30}Cr_{0.70})_{Σ2.00}^ZSi_{3.00}O_{10.50}OH_{3.50} for chromian pumpellyite-(Mg). Molecular water is absent in both minerals. The presence of silanol groups Si-OH is confirmed by Infrared (IR) spectroscopy. The existence of shuiskite as an individual mineral in its initial sense, *i.e.*, with Mg and Cr³⁺ dominant at the *X* and *Y* sites, respectively, is confirmed. The simplified formula of shuiskite has been refined: Ca₂(Mg,Cr)(Cr,Al)₂[SiO₄][Si₂O₆(OH,O)](OH,O)(OH)₂. The simplified formula of chromian pumpellyite-(Mg) is Ca₂(Mg,Cr)(Al,Cr)₂[SiO₄][Si₂O₆(OH,O)](OH,O)(OH)₂. In high-chromium pumpellyite-group minerals the preference of Cr for the *Y* site increases with increasing total Cr content: the distribution coefficient of Cr³⁺ between the *X* and *Y* sites, *K*_D = (Cr/Al)_X/(Cr/Al)_Y, is 2.79 in chromian pumpellyite-(Mg) and 1.85 in shuiskite.

Key-words: shuiskite; pumpellyite; chromium; silicate; crystal structure; infrared spectroscopy; Saranovskoe deposit; Urals.

1. Introduction

Pumpellyite-group minerals are typical rock-forming components of many low-grade metamorphic and hydrothermally altered rocks. The general formula of these minerals is ^{VII}W₂^{VI}X^{VI}Y₂^{IV}Z₃O_{14-n}(OH)_n (*Z* = 4), where the *W* and *Z* sites are occupied predominantly by Ca and Si, respectively, the *X* site can contain both divalent and trivalent cations Mg, Al, Mn²⁺, Mn³⁺, Fe²⁺, Fe³⁺, V³⁺ and Cr³⁺, whereas the *Y* site is occupied only by trivalent cations: Al, Mn³⁺, Fe³⁺, V³⁺ and Cr³⁺; Roman numerals mean coordination numbers (Passaglia & Gottardi, 1973). According to the IMA-accepted nomenclature (Passaglia & Gottardi, 1973), pumpellyite-group members are named according to the predominant cations in the *Y* (rootname) and *X* (suffix-modifier) sites. Minerals with predominant Al at the *Y* site have the root-name pumpellyite first proposed by Palache & Vassar (1925), Fe³⁺ – julgoldite (Moore, 1971), Cr³⁺ – shuiskite (Ivanov *et al.*, 1981), Mn³⁺ – okhotskite (Togari & Akasaka, 1987), and V³⁺ – poppiite (Brigatti *et al.*, 2006). For the species of the pumpellyite and

julgoldite series, the dominant cation at the *X* site is reflected in their names: pumpellyite-(Mg), pumpellyite-(Fe²⁺), julgoldite-(Fe³⁺), *etc.*; shuiskite, okhotskite and poppiite are minerals with only one known dominant cation at the *X* site for each.

Shuiskite was first described from the Biserskoe chromite deposit, Middle Urals, Russia and approved by the IMA CNMMN as a new mineral with the simplified formula Ca₂(Mg,Al)(Cr,Al)₂(SiO₄)(Si₂O₇)(OH)₂·H₂O (Ivanov *et al.*, 1981). Its crystal structure was not studied and this formula was based on the assumption that Cr³⁺ mainly occupies the *Y* site, while the actual distribution of Cr, Mg, Al and Fe at the *X* and *Y* sites had not been determined and it is formally possible to distribute these cations so that Cr would be subordinate in both *X* (Mg > Cr) and *Y* (Al > Cr) positions.

The first data on chromium distribution in pumpellyite-group minerals were obtained by Nagashima & Akasaka (2007) and Nagashima *et al.* (2010a and b). They examined a chromian variety of pumpellyite-(Mg), with the average Cr content of 14.4 wt% Cr₂O₃, from the Saranovskoe (Glavnoe

Saranovskoe) chromite deposit, Middle Urals, Russia, and showed that Cr was distributed between both *X* and *Y* sites, preferring the *X* site over the *Y* site. Hamada *et al.* (2010) studied the crystal chemistry of five samples of chromian pumpellyite from Osayama, Okayama Prefecture, Japan, with Cr contents in the range of 2.0–7.6 wt% Cr_2O_3 and confirmed that Cr occupies the *X* site rather than *Y*, and this tendency becomes stronger with increasing total Cr content. The implications of these data led to speculations on the validity of shuiskite as an individual mineral species, although its crystal chemistry has not hitherto been studied.

The aim of the present study is therefore: (1) to examine the crystal structures of the type specimen of shuiskite and, for comparison, a Cr-rich variety of pumpellyite-(Mg) with Cr content higher than in the sample reported by Nagashima & Akasaka (2007); (2) to examine the distribution of Cr over the octahedral sites in Cr-rich pumpellyite-group minerals; (3) to clarify the status of shuiskite; (4) to refine the simplified formula of shuiskite.

2. Specimens

The crystals of shuiskite from the Biserskoe deposit were selected for this study from the type specimen. It is deposited under catalogue no. 81684 in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow. It was provided in 1982 by O.K. Ivanov, the senior author of the original description of shuiskite (Ivanov *et al.*, 1981). In addition, we contacted Prof. Ivanov before our study and he confirmed this material as the type specimen of shuiskite. This mineral occurs in association with uvarovite as aggregates of dark violet-brown prismatic crystals up to 1 cm long on the wall of a fracture in massive chromitite (Fig. 1).

The specimen of the chromian pumpellyite-(Mg) was collected in 2016 by local miners at the Rudnaya underground mine operating at the Glavnoe Saranovskoe deposit and provided for our study by the prominent mineral collector O.S. Bartenev (Moscow). The mineral forms dark brownish-purple acicular crystals up to 1.5 cm long combined in sprays or sheaf-like aggregates. They overgrow walls of cracks in massive chromitite coated by thin crusts of pink Cr-bearing clinochlore. Typically, chromian pumpellyite-(Mg) is embedded in calcite, the latest mineral in this assemblage, which partially or completely fills the cracks.

Both Biserskoe and Glavnoe (Main) Saranovskoe deposits belong to the Saranovskaya group of chromite deposits located in the Perm Kray (the north-west part of the Middle Urals region). Biserskoe has another name, Yuzhno-Saranovskoe (= Southern Saranovskoe), while Glavnoe Saranovskoe is also known as Saranovskoe (= Saranovskii mine, or Sarany, or Sarani, after the town of Sarany within which this mine is situated). The Glavnoe Saranovskoe deposit is famous as a source of numerous world-class museum specimens of uvarovite and Cr-bearing varieties of titanite, amesite, diaspore, *etc.* The historical, geological and mineralogical data on the Saranovskaya group of chromite deposits were recently summarized by Ivanov (2016).



Fig. 1. Prismatic crystals of shuiskite up to 1 cm long in association with uvarovite on the wall of a fracture in massive chromitite. Specimen #81684. Field of view: 3 cm.

3. Experimental procedure

The chemical composition of shuiskite and chromian pumpellyite-(Mg) (Table 1) was studied in the Institute of Experimental Mineralogy RAS using a CamScan MV2300 scanning electron microscope equipped with ED spectrometer INCA Energy 350, under the following conditions: operating voltage 20 kV and beam current 1.0 nA. The following standards were used: SiO_2 ($\text{SiK}\alpha$), MgO ($\text{MgK}\alpha$), wollastonite ($\text{CaK}\alpha$), Al_2O_3 ($\text{AlK}\alpha$), Ti ($\text{TiK}\alpha$), Cr ($\text{CrK}\alpha$).

Infrared (IR) absorption spectra were obtained from powdered samples mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1} ; 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Crystal-structure studies were carried out using single-crystal diffraction data collected in a full sphere of the reciprocal space on an Xcalibur S diffractometer equipped with a CCD detector at $T = 293 \text{ K}$. The measured intensities were corrected for Lorentz, background, polarization and absorption effects.

Both crystal structures reported here were solved by direct methods and refined by full-matrix least-squares techniques on F^2 in space group $C2/m$ using the SHELX-97 program package (Sheldrick, 2015). The crystal data, the details of the X-ray diffraction experiments and the structure refinement parameters are given in Table 2.

The crystal structures of shuiskite and chromian pumpellyite-(Mg) were refined to the R_1 values of 3.00 and 3.13% on the basis of 1924 and 2011 unique reflections with $I > 2\sigma(I)$, respectively.

4. Results

Chemical data for shuiskite and chromian pumpellyite-(Mg) samples used for the structure determination are given in Table 1. The averaged empirical formulae calculated on

Table 1. Chemical composition (wt%) of shuiskite and chromian pumpellyite-(Mg).

	Shuiskite		Pumpellyite-(Mg)	
	Mean	Range (<i>n</i> = 4)	Mean	Range (<i>n</i> = 3)
SiO ₂	35.00	34.44–35.34	35.28	34.59–36.03
TiO ₂	–		0.67	0.56–0.76
Al ₂ O ₃	10.27	9.89–10.9	14.28	13.17–14.99
Cr ₂ O ₃	22.62	21.87–23.12	16.36	15.64–17.50
MgO	3.64	3.23–3.99	3.97	3.46–4.40
CaO	22.27	21.61–22.69	23.28	22.87–23.53
H ₂ O*	6.21		6.48	
Total	100.01		100.32	
Atoms per formula unit (based on 8 cations)				
Si	2.97		2.93	
Ti	–		0.04	
Al	1.03		1.40	
Cr	1.51		1.07	
Mg	0.46		0.49	
Ca	2.03		2.07	
OH*	3.52		3.59	
O*	10.48		10.41	

*OH[−]/O^{2−} ratio in formulae and H₂O content (in wt%) are calculated by charge balance for O+OH = 14 *p.f.u.*

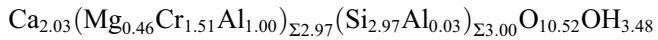
Table 2. Crystal data, data collection information and structure refinement details for shuiskite and chromian pumpellyite-(Mg).

Sample	Shuiskite	Pumpellyite-(Mg)
Space group, <i>Z</i> *	<i>C</i> 2/ <i>m</i> , 4	<i>C</i> 2/ <i>m</i> , 4
<i>a</i> , Å	19.2156(7)	19.1776(8)
<i>b</i> , Å	5.9779(2)	5.9537(3)
<i>c</i> , Å	8.8268(3)	8.8282(4)
β, °	97.785(3)	97.668(4)
<i>V</i> , Å ³	1004.59(6)	998.97(8)
λ (MoKα) (Å), <i>T</i> (K)	0.71073, 293(2)	
Diffractometer	Xcalibur S CCD	
Reflections collected	13489	13343
Unique reflections, <i>R</i> _{int}	2253, 0.0509	2270, 0.0458
Reflections with <i>I</i> > 2σ(<i>I</i>)	1924	2011
Refined parameters	123	123
<i>R</i> ₁	0.0301	0.0312
w <i>R</i> _{2all} (<i>F</i> ²)	0.0832	0.0760
GoF	1.055	1.001
Δρ _{max} /Δρ _{min} (e/Å ³)	0.974/−0.642	0.905/−0.551

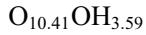
*For formulae given in Table 1.

the basis of 8 cations (with the OH[−]/O^{2−} ratio calculated by charge balance for O + OH = 14 per formula unit, *p.f.u.*; H₂O molecules were not involved based on the structural and IR spectroscopy data: see below) are:

Shuiskite [based on four spot analyses]



Chromian pumpellyite-(Mg) [based on three spot analyses]



Atom coordinates, equivalent thermal displacement parameters, site occupancy factors (or refined site-scatterings), and bond-valence sums are given in Table 3, selected interatomic distances in Table 4 and anisotropic thermal displacement parameters in Table S1, freely available as Supplementary Material linked to this article at <https://pubs.geoscienceworld.org/eurjmin/>, along with the CIF files. Anion sites are labelled after Hamada *et al.* (2010).

The crystal structures of shuiskite and chromian pumpellyite-(Mg) are based on a pair of chains of edge-sharing octahedra $X\text{O}_6$ and $Y\text{O}_6$ (where X and Y = Al³⁺, Cr³⁺, Mg²⁺) running parallel to [010], which are linked together via ortho- and disilicate groups, and Ca-centered polyhedra (Fig. 2).

In both minerals Cr³⁺ is distributed between the X and Y sites. In shuiskite the X site is occupied by 0.46Mg + 0.36Cr + 0.18Al with the refined number of electrons (*e*_{ref}) of 16.9 and the average $\langle X\text{--O} \rangle$ distance of 2.024 Å, while the site occupancy at the Y site was refined to 52% Cr and 48% Al (*e*_{ref} = 18.7) with the average $\langle Y\text{--O} \rangle$ distance of 1.957 Å. In chromian pumpellyite-(Mg) the X site is occupied by 0.5Mg + 0.3Cr + 0.2Al (*e*_{ref} = 6.9) and the average $\langle X\text{--O} \rangle$ distance of 2.016 Å, while the occupancy at the Y site is 65% Al and 35% Cr (*e*_{ref} = 16.6) with the average $\langle Y\text{--O} \rangle$ distance of 1.946 Å (Tables 3–4). For comparison, in chromian pumpellyite studied by Nagashima *et al.* (2010b), the X site is occupied by 0.49Mg + 0.28Cr + 0.23Al with the average $\langle X\text{--O} \rangle$ distance of 2.007 Å, while the Y site is occupied by 0.74Al + 0.26Cr with the average $\langle Y\text{--O} \rangle$ distance of 1.936 Å. The sizes of both $X\text{O}_6$ and $Y\text{O}_6$ octahedra increase with increasing total Cr content. The bond-valence sums (BVS) at the X site are 2.50 valence units (*vu*) in shuiskite and 2.54 *vu* in pumpellyite-(Mg), which is in a good agreement with the partial $M^{3+} \rightleftharpoons M^{2+}$ substitution at the X site (Table 3).

The BVS at the O(5) and O(7) sites are, respectively, 1.04 and 1.04 *vu* in shuiskite, and 1.04 and 1.06 *vu* in pumpellyite-(Mg), indicating that these sites are occupied by hydroxyl groups, while the O(10) and O(11) sites have mixed O/OH occupancies [1.30 and 1.38 *vu* in shuiskite and 1.30 and 1.39 *vu* in pumpellyite-(Mg)] (Table 3). The mixed occupancy at the O(10) means that disilicate [Si₂O₆(OH,O)] groups but not [Si₂O₇] are present in both minerals. The remaining ten anion sites are occupied by O in both cases. The BVS indicate that the presence of H₂O⁰ as a dominant constituent in any site of the studied samples is hardly probable.

Both shuiskite and chromian pumpellyite-(Mg) show rather strong IR bands of O–H-stretching (in the range from 3000 to 3600 cm^{−1}), Si–O-stretching (900–1100 cm^{−1}), as well as O–Si–O and Si–O–Si bending (below 650 cm^{−1}) vibrations (Fig. 3). The bands at 836–842 cm^{−1} and, possibly, the weak bands at 681–682 cm^{−1} are tentatively assigned to $M\cdots\text{O}\text{--H}$ modes (where M is a metal cation in X or Y site), but these bands may correspond to mixed vibrations involving $M\cdots\text{O}\text{--H}$ angles and silicate groups. The weak bands at 1110–1115 and 1930–1935 cm^{−1} correspond to overtones or combination modes. The origin of the weak

Table 3. Atom coordinates (x, y, z), equivalent thermal displacement parameters (U_{eq} , Å 2), site occupancy factors (s.o.f.) and bond-valence sums (BVS) in the structures of shuiskite (upper line) and chromian pumpellyite-(Mg) (lower line).

Site	x	y	z	U_{eq}	s.o.f./site composition	BVS ³
Ca(1)	0.33930(3)	1/2	0.25093(6)	0.01008(11)	1	2.20
	0.33947(3)	1/2	0.25065(6)	0.00924(10)		2.19
Ca(2)	0.15472(3)	1/2	0.18823(7)	0.01313(12)	1	2.09
	0.15458(3)	1/2	0.18849(7)	0.01223(11)		2.08
X	1/4	1/4	1/2	0.00665(12)	[16.6] Mg _{0.46} Cr _{0.36} Al _{0.18} ¹	2.50
	1/4	1/4	1/2	0.00596(12)		[15.8] Mg _{0.50} Cr _{0.30} Al _{0.20} ²
Y	0.495426(18)	0.24689(5)	0.25406(4)	0.00569(12)	[18.7] Cr _{0.518(4)} Al _{0.482(5)}	2.94
	0.49551(2)	0.24678(7)	0.25439(4)	0.00501(12)		[16.9] Al _{0.651(5)} Cr _{0.349(4)}
Si(1)	0.09103(3)	0	0.05091(8)	0.00675(13)	1	3.95
	0.09060(4)	0	0.05098(8)	0.00601(13)		3.97
Si(2)	0.24794(4)	0	0.16550(8)	0.00763(13)	1	3.82
	0.24790(4)	0	0.16564(8)	0.00670(13)		3.82
Si(3)	0.40231(3)	0	0.46555(8)	0.00672(13)	1	3.84
	0.40247(4)	0	0.46547(8)	0.00606(13)		3.82
O(1)	0.07295(7)	0.2237(2)	0.13751(15)	0.0094(2)	1	2.02
	0.07242(7)	0.2243(2)	0.13755(15)	0.0087(2)		2.02
O(2)	0.24623(6)	0.2298(2)	0.26535(15)	0.0098(2)	1	1.93
	0.24626(7)	0.2304(2)	0.26570(15)	0.0094(2)		1.93
O(3)	0.41549(7)	0.2221(2)	0.36701(16)	0.0098(2)	1	1.85
	0.41601(7)	0.2223(2)	0.36698(15)	0.0093(2)		1.85
O(4)	0.44435(9)	1/2	0.1303(2)	0.0077(3)	1	2.02
	0.44474(9)	1/2	0.1304(2)	0.0072(3)		1.99
O(5) = OH	0.45720(9)	0	0.1285(2)	0.0101(3)	1	1.04
	0.45754(10)	0	0.1299(2)	0.0097(3)		1.04
O(6)	0.04478(9)	1/2	0.3703(2)	0.0082(3)	1	1.98
	0.04488(10)	1/2	0.3702(2)	0.0077(3)		1.96
O(7) = OH	0.03423(10)	0	0.3724(2)	0.0123(4)	1	1.04
	0.03361(11)	0	0.3704(2)	0.0110(3)		1.06
O(8)	0.17625(9)	0	0.0353(2)	0.0101(3)	1	2.01
	0.17598(10)	0	0.0361(2)	0.0096(3)		2.02
O(9)	0.17602(9)	1/2	0.4759(2)	0.0110(3)	1	1.91
	0.17649(10)	1/2	0.4767(2)	0.0110(3)		1.90
O(10) = OH,O	0.31337(10)	0	0.0668(2)	0.0146(4)	1	1.30
	0.31339(10)	0	0.0665(2)	0.0139(4)		1.30
O(11) = OH,O	0.18445(9)	0	0.4975(2)	0.0101(3)	1	1.38
	0.18476(10)	0	0.4975(2)	0.0098(3)		1.39

¹The X site in shuiskite was refined assuming full occupancy and refining Mg (including the similarly light Al) against Cr, the best agreement was obtained with Mg_{0.618(5)}Cr_{0.382(5)}. In the final refinement cycles the occupancy was fixed as Mg_{0.46}Cr_{0.36}Al_{0.18} based on e_{ref} values (given in square brackets), electron microprobe data and BVS;

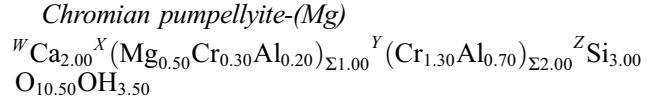
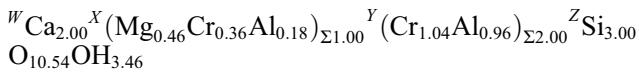
²The X site in chromian pumpellyite-(Mg) was refined assuming full occupancy and refining Mg (including the similarly light Al) against Cr, the best agreement was obtained with Mg_{0.678(5)}Cr_{0.322(5)}. In the final refinement cycles the occupancy was fixed as Mg_{0.50}Cr_{0.30}Al_{0.20} based on e_{ref} values, electron microprobe data and BVS;

³BVS have been calculated taking into account s.o.f., parameters are taken from Brese & O'Keeffe (1991).

bands at 2207–2210 cm $^{-1}$ is unclear. Their wavenumbers are too high for a first overtone or combination mode. The presence of these bands in the IR spectra can be explained by the presence of silanol groups Si–OH, confirming structural data that show significant protonation of O(10). Absorption bands in the range 1600–1700 cm $^{-1}$, which are due to H–O–H bending vibrations, are not observed, indicating that molecular water is absent in both shuiskite and chromian pumpellyite-(Mg).

The formulae obtained from the structural refinements ($Z = 4$) are in a good agreement with electron microprobe data:

Shuiskite



5. Discussion

Our data show that Cr $^{3+}$ in shuiskite is the prevailing cation at the Y site and Mg at the X site, which confirms (1) the individuality of shuiskite as a mineral species, the only well-studied ^YCr -dominant member of the pumpellyite group, and (2) the correctness of the distribution of the dominant cations at the X and Y sites in the original formula of shuiskite proposed by Ivanov *et al.* (1981): Ca₂(Mg,Al)(Cr,Al)₂(SiO₄)(Si₂O₇)(OH)₂·H₂O. At the same time, the

Table 4. Selected interatomic distances (\AA) for shuiskite and chromian pumpellyite-(Mg).

		Shuiskite	Pumpellyite-(Mg)
Ca(1)	O(11)	2.3270(19)	O(11) 2.332(2)
	O(3)	2.3552(13) \times 2	O(3) 2.3540(14) \times 2
	O(4)	2.4062(18)	O(4) 2.4027(19)
	O(2)	2.4261(13) \times 2	O(2) 2.4193(14) \times 2
	O(8)	2.5033(19)	O(8) 2.509(2)
<Ca(1)-O>		2.400	2.399
Ca(2)	O(1)	2.2818(13) \times 2	O(1) 2.2780(14) \times 2
	O(10)	2.412(2)	O(2) 2.4111(13) \times 2
	O(2)	2.4167(13) \times 2	O(10) 2.411(2)
	O(9)	2.517(2)	O(9) 2.523(2)
	O(6)	2.8221(18)	O(6) 2.810(2)
<Ca(2)-O>		2.450	2.446
X	O(11)	1.9526(11) \times 2	O(11) 1.9427(12) \times 2
	O(9)	2.0536(12) \times 2	O(9) 2.0416(13) \times 2
	O(2)	2.0662(13) \times 2	O(2) 2.0635(13) \times 2
<X-O>		2.024	2.016
Y	O(1)	1.9297(13)	O(7) 1.9122(12)
	O(5)	1.9302(12)	O(1) 1.9170(14)
	O(7)	1.9302(12)	O(5) 1.9192(13)
	O(3)	1.9470(13)	O(3) 1.9335(14)
	O(6)	1.9663(12)	O(6) 1.9601(12)
	O(4)	2.0385(12)	O(4) 2.0332(13)
<Y-O>		1.957	1.946
Si(1)	O(1)	1.6017(13) \times 2	O(1) 1.6003(14) \times 2
	O(4)	1.6512(19)	O(4) 1.654(2)
	O(8)	1.6619(18)	O(8) 1.660(2)
<Si(1)-O>		1.629	1.629
Si(2)	O(10)	1.624(2)	O(10) 1.624(2)
	O(2)	1.6348(13) \times 2	O(2) 1.6340(14) \times 2
	O(8)	1.6704(19)	O(8) 1.6701(19)
<Si(2)-O>		1.641	1.641
Si(3)	O(3)	1.6256(13) \times 2	O(3) 1.6232(14) \times 2
	O(6)	1.6538(19)	O(6) 1.6535(19)
	O(9)	1.6563(18)	O(9) 1.661(2)
<Si(3)-O>		1.640	1.640

anionic part of this formula should be corrected in the light of the newly obtained data.

Hamada *et al.* (2010) showed that Cr occupancies at the X and Y sites in pumpellyite with Cr contents in the range of 2.0–7.6 wt% Cr_2O_3 (0.13–0.49 *apfu* Cr) are correlated with total Cr content in the pumpellyite (Cr_{total} , *apfu* in the formula based on 32 atoms of metals + Si, $Z = 1$): $\text{Cr}_X = 0.3258\text{Cr}_{\text{total}} + 0.048$, $\text{Cr}_Y = 0.674\text{Cr}_{\text{total}} - 0.051$, and $(\text{Cr}/\text{Al})_X$ and $(\text{Cr}/\text{Al})_Y$ are correlated with Cr_{total} by the relationships $(\text{Cr}/\text{Al})_X = 0.1167(\text{Cr}_{\text{total}})^2 - 0.0142\text{Cr}_{\text{total}} + 0.1165$ and $(\text{Cr}/\text{Al})_Y = 0.1233\text{Cr}_{\text{total}} - 0.0344$. According to calculations in our chromian pumpellyite-(Mg), $\text{Cr}_X = 1.20$ from structural data [and 1.35 calculated], and $\text{Cr}_Y = 2.80$ [2.65], while in shuiskite $\text{Cr}_X = 1.44$ [1.87] and $\text{Cr}_Y = 4.16$ [3.72]. The distribution coefficient of chromium between the X and Y sites, $K_D = (\text{Cr}/\text{Al})_X/(\text{Cr}/\text{Al})_Y$, is 2.79 from our structural data and 4.20 calculated using Cr_X and Cr_Y in chromian pumpellyite-(Mg) and 1.85 [5.64 calculated] in shuiskite. Although our data corroborate the idea that Cr prefers the X site over Y in pumpellyite-group minerals (Nagashima & Akasaka, 2007; Nagashima *et al.* (2010b);

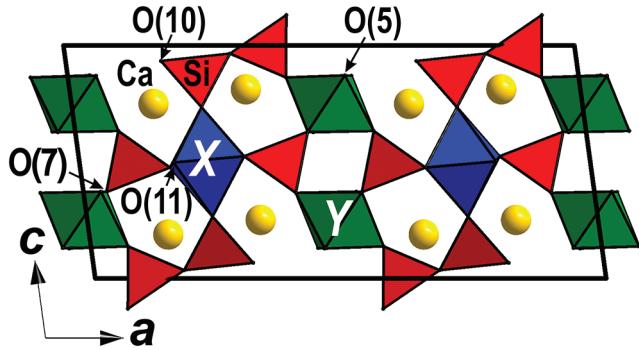


Fig. 2. General view of the crystal structure of shuiskite. Anion sites with full or partial OH occupancies are labelled. Unit cell is outlined.

Hamada *et al.*, 2010), the preference of Cr for the X site actually decreases with increasing total Cr content (Table 5). It allows Cr to become the predominant cation at the Y site in shuiskite. Moreover, although all structurally studied Cr-rich pumpellyite-group minerals are characterised by a relatively constant Mg content, and the main substitution mechanism is $\text{Al} \rightarrow \text{Cr}$ (Fig. 4a), the actual distribution of the main octahedral cations (Mg, Al, and Cr) at the X site does not follow a certain pattern (Fig. 4b). Thus, it would not be advisable to use the formulae suggested by Hamada *et al.* (2010) to calculate the distribution of Cr in pumpellyite-group minerals with a high content of Cr.

A similar dual distribution of Cr^{3+} was observed in tourmalines $X_{0-1}\text{Y}_3\text{Z}_6(\text{IV}T_6\text{O}_{18})(\text{BO}_3)_3V_3W$, where at low Cr content Cr essentially occupies the Y octahedra, replacing divalent cation Mg, and then, when the Cr content increases further, Cr occupies the Z octahedra, replacing trivalent cations (Vereshchagin *et al.*, 2014).

Thus, the simplified formula of shuiskite, $\text{Ca}_{2.00}(\text{Mg}_{0.46}\text{Cr}_{0.36}\text{Al}_{0.18})_{\Sigma 1.00}(\text{Cr}_{1.04}\text{Al}_{0.96})_{\Sigma 2.00}\text{Si}_{3.00}\text{O}_{10.54}\text{OH}_{3.46}$, originally proposed as $\text{Ca}_2(\text{Mg},\text{Al})(\text{Cr},\text{Al})_2(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})_2\cdot\text{H}_2\text{O}$ (Ivanov *et al.*, 1981) should be refined as follows: $\text{Ca}_2(\text{Mg},\text{Cr})(\text{Cr},\text{Al})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH},\text{O})](\text{OH},\text{O})(\text{OH})_2$, taking into account: (1) the distribution of Cr, Mg and Al between the X and Y sites, (2) the presence of silanol groups $\text{Si}-\text{OH}$, (3) the absence of H_2O molecules, and (4) the presence of OH groups, besides the O(5) and O(7) sites, also in O(10) and O(11): roughly 1.5 OH *pfa* are distributed between O(10) and O(11). The simplified structural formula of shuiskite can be written as: $\text{Ca}^{(1)}\text{Ca}^{(2)}\text{Ca}^X(\text{Mg},\text{Cr})(\text{Cr},\text{Al})_2[\text{Si}^{(3)}\text{SiO}_4][\text{Si}^{(1)}\text{Si}^{(2)}\text{Si}_2\text{O}_6\text{O}^{(10)}(\text{OH},\text{O})]\text{O}^{(11)}(\text{OH},\text{O})^{(5)}\text{O}^{(7)}(\text{OH})_2$. The simplified formula of the studied chromian pumpellyite-(Mg), $\text{Ca}_{2.00}(\text{Mg}_{0.50}\text{Cr}_{0.30}\text{Al}_{0.20})_{\Sigma 1.00}(\text{Al}_{1.30}\text{Cr}_{0.70})_{\Sigma 2.00}\text{Si}_{3.00}\text{O}_{10.50}\text{OH}_{3.50}$, is $\text{Ca}_2(\text{Mg},\text{Cr})(\text{Al},\text{Cr})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH},\text{O})](\text{OH},\text{O})(\text{OH})_2$.

According to IR spectroscopic data (Fig. 3) molecular water is absent in both shuiskite and chromian pumpellyite-(Mg), although water molecules are present in most samples of pumpellyite-group minerals with high amounts of divalent octahedral cations. Usually the band of H–O–H bending vibrations in their IR spectra is very weak. The strongest band in the range of 1620–1660 cm^{-1} is observed

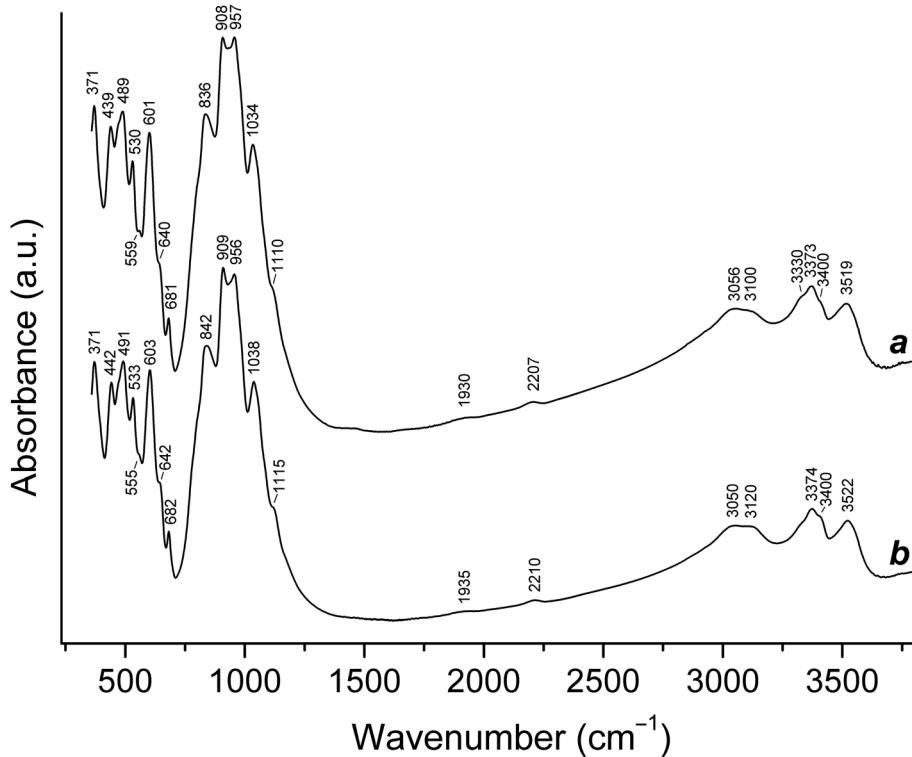


Fig. 3. Powder IR spectra of (a) shuiskite and (b) chromian pumpellyite-(Mg).

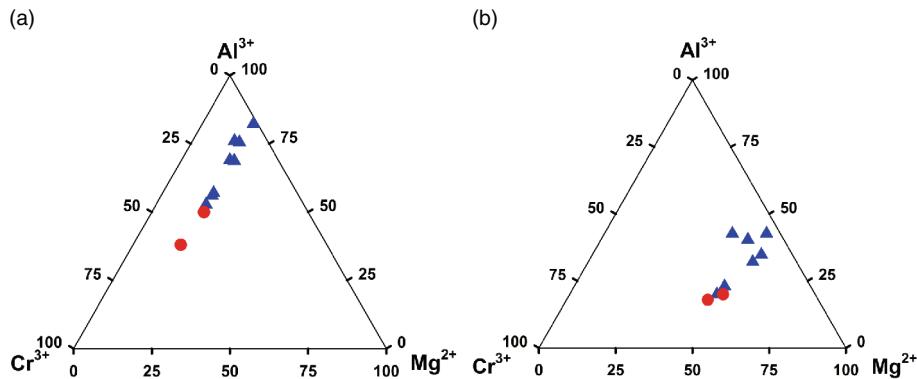


Fig. 4. Ternary diagrams of the main octahedral cations in chromium-bearing pumpellyite-group minerals (a) and at the *X* sites in their structures (b). Circles – present study; triangles – previous works (same sources as in Table 5).

in the IR spectrum of pumpellyite-(Mn²⁺) from the Bikulovskoe manganese deposit, South Urals (Chukanov, 2014).

The replacement of Mg by Cr³⁺ and Al at the *X* site in pumpellyite-group minerals is likely to proceed according to the substitution mechanism $Mg^{2+} + OH^- \rightarrow (Cr,Al)^{3+} + O^{2-}$ with corresponding anion substitutions at the O(11) site, as it was suggested by Yoshiasa & Matsumoto (1985).

6. Conclusions

The results of this study on shuiskite with 21.9–23.1 wt% Cr₂O₃ (1.45–1.56 apfu Cr) from its type locality, the

Biserskoe (Yuzhno-Saranovskoe) deposit, confirm its existence as an individual mineral species in its initial sense, *i.e.*, with Mg as the predominant cation at the *X* site and Cr³⁺ at the *Y* site, and allow us to refine the shuiskite formula in its anionic part as follows: Ca₂(Mg,Cr)(Cr,Al)₂[SiO₄][Si₂O₆(OH,O)](OH,O)(OH)₂.

Structural study is mandatory for the reliable identification of shuiskite in samples with cation compositions close to the possible border with pumpellyite(s). The specimens with Cr contents up to 17.5 wt% Cr₂O₃ (1.14 apfu Cr) were reliably identified as chromian pumpellyite based on chemical composition (Nagashima & Akasaka, 2007; Nagashima *et al.*, 2010a and b; Hamada *et al.*, 2010; this work).

Table 5. Contents of main octahedral cations (Mg, Al, Cr³⁺), distribution of Cr between X and Y sites, and distribution coefficient (K_D) for Cr in chromium-bearing pumpellyite-group minerals—shuiskite (bottom row) and pumpellyite (other rows).

Cr, apfu ¹	Al, apfu ¹	Mg, apfu ¹	Cr, % ²		K_D ³	References
			X	Y		
0.04	2.36	0.47	4	0	—	Hamada <i>et al.</i> , 2010
0.27	2.22	0.45	11	8	3.09	
0.31	2.25	0.40	15	8	4.54	
0.41	1.99	0.49	10	16	1.66	
0.45	2.00	0.45	12	16	1.79	
0.94	1.58	0.48	32	31	3.56	Nagashima & Akasaka, 2007
0.83	1.68	0.49	31	26	4.39	Nagashima <i>et al.</i> , 2010a
0.80	1.71	0.49	29	26	3.68	Nagashima <i>et al.</i> , 2010b
1.00	1.50	0.50	30	35	2.79	
1.40	1.14	0.46	36	52	1.87	This work

¹Cr, Al, and Mg contents refined from the structural data, apfu calculated on the basis of 8 cations;

²Share of Cr in the content of the X and Y sites;

³ $K_D = (\text{Cr}/\text{Al})_X/(\text{Cr}/\text{Al})_Y$.

At low Cr content in pumpellyites, Cr essentially occupies X octahedra and the preference of Cr for the X site increases with increasing total Cr content (Hamada *et al.*, 2010). However, the dependence is reversed when the Cr content further increases. The distribution coefficient of chromium between the X and Y sites, $K_D = (\text{Cr}/\text{Al})_X/(\text{Cr}/\text{Al})_Y$, decreases, allowing Cr to become the predominant cation at the Y site, resulting in the formation of shuiskite.

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