Feodosiyite, $Cu_{11}Mg_2Cl_{18}(OH)_8 \cdot 16H_2O$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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With 6 figures and 7 tables

Abstract: A new mineral feodosiyite $Cu_{11}Mg_2Cl_{18}(OH)_8 \cdot 16H_2O$ is found in the Glavnaya Tenoritovaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Closely associated minerals are belloite, avdoninite, sylvite, carnallite, chlorothionite, and dioskouriite. Feodosiyite forms tabular or prismatic crystals up to $0.02 \times 0.1 \times 0.1 \, mm^3$ combined in interrupted incrustations up to $0.1 \times 0.5 \times 1 \, cm^3$ overgrowing basalt scoria. The mineral is transparent, bright green, with vitreous lustre. Feodosiyite is brittle. Its Mohs' hardness is *ca* 3. One direction of imperfect cleavage was observed, the fracture is uneven. $D_{meas} = 2.57(1)$, $D_{calc} = 2.563 \, g \, cm^{-3}$. Feodosiyite is optically biaxial (−), $\alpha = 1.660(3)$, $\beta = 1.690(5)$, $\gamma = 1.718(5)$, $2V_{meas} = 90(5)°$. The Raman spectrum is reported. The chemical composition (wt.%, electron-microprobe data, H_2O calculated by total difference) is: MgO 5.39 (4.84−5.91), Cu 46.98, Cl 35.42, H_2O_{calc} 20.21, −O = Cl −8.00, total 100.00. The empirical formula calculated based on 42 atoms O+Cl *pfu* is: $Cu_{10.58}Mg_{2.40}Cl_{17.90}(OH)_{8.06} \cdot 16.04H_2O$. Feodosiyite is monoclinic, $P2_1/c$, $a = 12.9010(6)$, $b = 16.4193(5)$, $c = 11.9614(5)$ Å, $\beta = 113.691(6)°$, $V = 2320.20(17)$ Å^3 and $Z = 2$. The strongest reflections of the powder XRD pattern $[d,Å(I)(hkl)]$ are: 11.87(100)(100), 6.585(15)(021), 5.969(25)(−102), 5.905(16)(200), 5.231(13)(121), 3.135(8) (222, −412, −151) and 2.924(11)(−333, −251). The crystal structure, solved from single-crystal XRD data $[R1(F) = 0.0867]$, is unique. It is based on layers of Cu^{2+}-centred polyhedra. Cu^{2+} cations occupy six crystallographically non-equivalent sites that are placed in distorted octahedra $Cu(1,3,5)(OH)_2Cl_4$, $Cu(2)(OH)_3Cl_3$, and $Cu(6)(OH)_2(H_2O)Cl_3$ and distorted tetragonal pyramids $Cu(4)(OH)_2Cl_3$. Isolated almost regular $Mg(H_2O)_6$ octahedra, linked with the layers of Cu-centred polyhedra by H-bonds, occur in the interlayer space, as well as separate H_2O molecules. The mineral is named in honour of the outstanding Russian geologist Feodosiy Nikolaevich Chernyshev (1856−1914).

Key words: feodosiyite, new mineral, copper magnesium chloride, crystal structure, fumarole; Tolbachik volcano, Kamchatka

Introduction

Chloride mineralization is very common for fumaroles related to active volcanoes. Chlorides are known in fumarolic deposits of almost all known types. They crystallize in a wide temperature range and occur in different mineral associations. Very specific chloride-bearing assemblages form in the upper zones of active fumaroles where minerals mainly crystallize not in the result of direct deposition from gaseous phase but as products of the interactions involving earlier formed, high-temperature sublimate minerals, volcanic gas and atmospheric components (at first, water or water vapour) at temperatures typically varying from 70 to 150 °C. The mineral-forming processes in these zones could be conditionally called "mixed, endogene-supergene" ones. Many minerals crystallized in these moderately hot zones contain H_2O or/and OH^-. This is an essential difference between this mineralization and assemblages formed in hot ($> 200 − 300$ °C) inner parts of the fumarole systems, in which only H-free phases appear. The uniqueness of the physical and chemical conditions of this subformation of he fumarolic formation gives rise to the originality of mineralization formed here.

Probably the brightest, in the aspect of diversity of chlorine minerals, example of such object is the Glavnaya Tenoritovaya ("Major Tenorite") fumarole at the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (NB

GTFE) of 1975–1976 (55° 41′ N, 160° 14′ E, 1200 m asl.) located 18 km SSW of the active volcano Ploskiy Tolbachik in Kamchatka, Russia. This fumarole, actively studied by us in 2012–2016, is the type locality of seven chlorides, namely sanguite $KCuCl_3$ (PEKOV et al. 2015a), chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$ (PEKOV et al. 2015b), mellizinkalite $K_3Zn_2Cl_7$ (PEKOV et al. 2015c), flinteite K_2ZnCl_4 (PEKOV et al. 2015d), romanorlovite $K_{11}Cu_9Cl_{25}(OH)_4 \cdot 2H_2O$ (PEKOV et al. 2016b, ZUBKOVA et al. 2016), dioskouriite $CaCu_4Cl_6(OH)_4 \cdot 4H_2O$ (PEKOV et al. 2016c), and described in the present paper feodosiyite $Cu_{11}Mg_2Cl_{18}(OH)_8 \cdot 16H_2O$. All these minerals were discovered in the upper part of the fumarole and had definitely crystallized under the above-mentioned conditions. It also seems interesting to highlight their crystal chemical originality: five of them (except of sanguite and flinteite) represent novel, unique structure archetypes. Other Cl minerals found by us in the same zone of the Glavnaya Tenoritovaya fumarole are avdoninite $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$ (PEKOV et al. 2016a), belloite $CuCl(OH)$, eriochalcite $CuCl_2 \cdot 2H_2O$, mitscherlichite $K_2CuCl_4 \cdot 2H_2O$, chlorothionite $K_2Cu(SO_4)Cl_2$, kainite $KMg(SO_4)Cl \cdot 3H_2O$, sylvite KCl, halite NaCl, and carnallite $KMgCl_3 \cdot 6H_2O$.

The new mineral feodosiyite (Cyrillic: феодосиит) is named in honour of the outstanding Russian geologist Feodosiy Nikolaevich Chernyshev (1856–1914), Academician of Russian Academy of Sciences and Director of Russian Geological Committee in 1903–1914. Both the mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2015–063). The type specimen (hermetically sealed in glass vial) is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 95278.

Occurrence and general appearance

The Second scoria cone of the NB GTFE is a monogenetic volcano about 300 m high and approximately 0.1 km³ in volume formed in 1975 (FEDOTOV & MARKHININ 1983) and demonstrates strong fumarolic activity to date. The Glavnaya Tenoritovaya fumarole located in the western wall of a big contraction fracture, so-called Micrograben, cross-cutting the summit of the scoria cone in the near-meridional direction. This fumarole is described by PEKOV et al. (2015a, 2016a).

The type specimen of feodosiyite was found in July 2014 in the outer, moderately hot sulfate-chloride zone, that occurs as a lenticular body about 1.5 m long and up to 0.2 m thick, on the northern flank of the fumarole. The temperature measured by us, using chromel-alumel

thermocouple, in this zone during collecting was about 100 °C. Feodosiyite is closely associated with belloite, avdoninite, sylvite, carnallite, chlorothionite, and dioskouriite. Other associated minerals are eriochalcite, halite, mitscherlichite, sanguite, chrysothallite, romanorlovite,
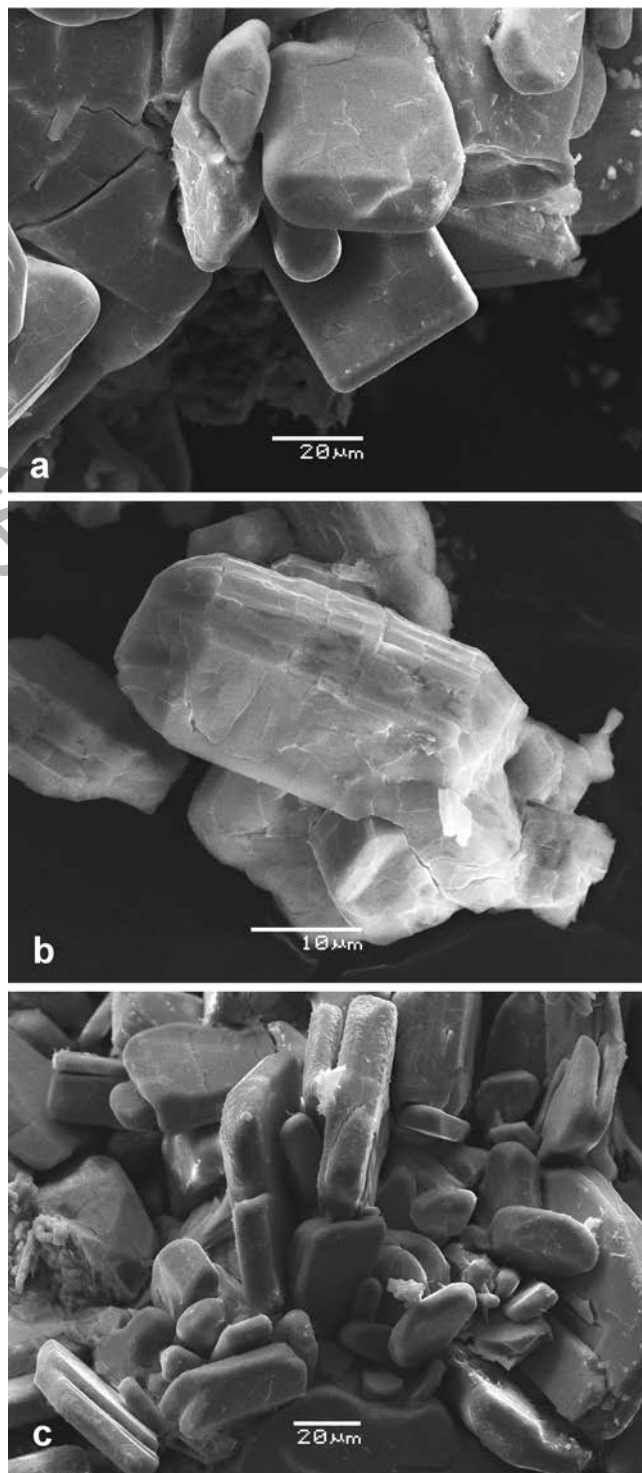
Fig. 1. Morphology of feodosiyite: a – tabular crystals, b – prismatic crystal, c – typical crystal group. SEM (SE) image.
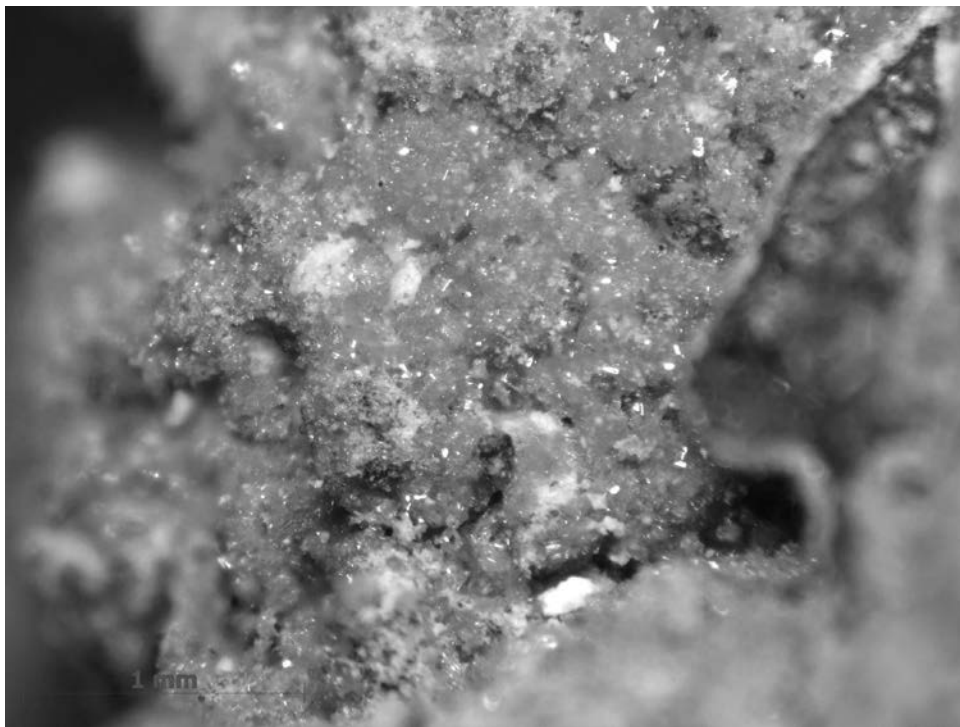
Fig. 2. Incrustation of bright green small crystals of feodosiyite on basalt scoria. FOV width 3.4 mm. Photo: I.V. PEKOV & A.V. KASATKIN.
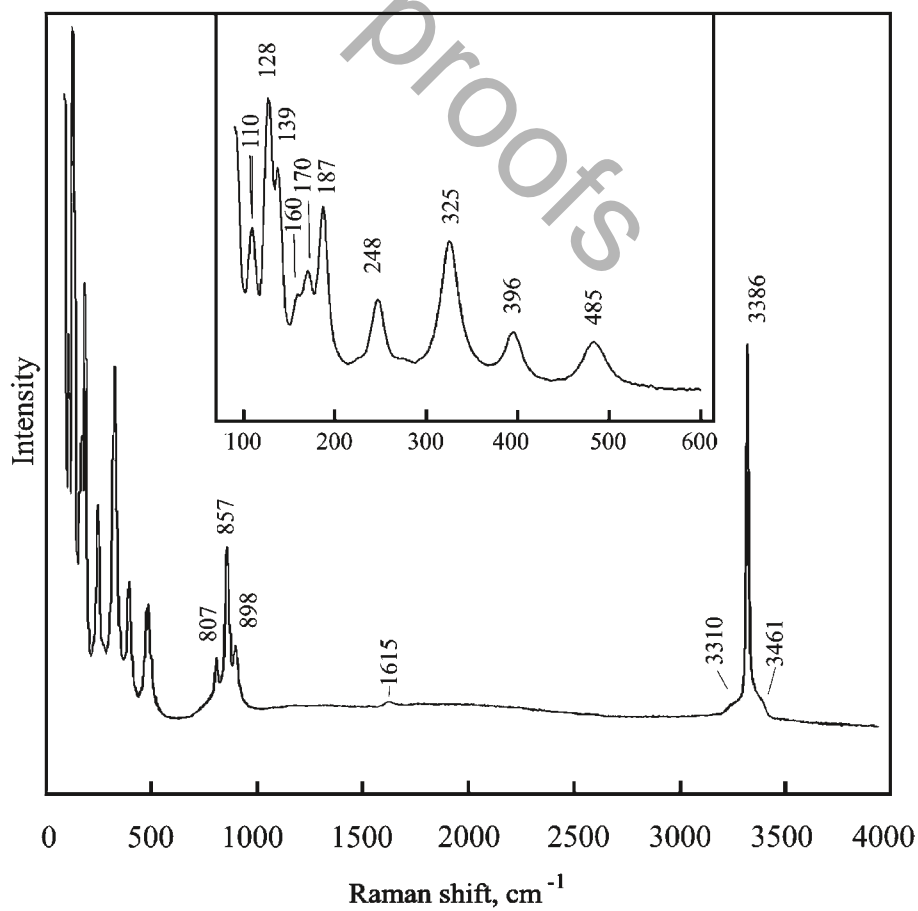

Fig. 3. The Raman spectrum of feodosiyite; an enlarged insert shows the low-frequency region.

Table 1. Powder X-ray diffraction data of feodosiyite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	$h\,k\,l$
100	11.87	100	11.814	100
1	9.62	0.5	9.590	110
1	8.81	0.5	8.771	−111
15	6.585	14	6.569	021
25	5.969	20	5.967	−102
16	5.905	5	5.907	200
4	5.572	2	5.608	−112
13	5.231	11	5.231	121
6	5.183	4	5.188	−202
1	5.030	1	5.037	−221
1	4.565	1	4.556	022
6	4.116	6	4.105	040
2	3.950	2	3.945	221
4	3.868	3	3.871	032
5	3.817	4	3.806	−321
1	3.645	0.5	3.642	−322
1	3.574	0.5	3.572	−123
1	3.513	1	3.508	−223
1	3.388	0.5, 0.5	3.404, 3.384	132, −313
1	3.338	1	3.336	023
4	3.190	4	3.187	−323
8	3.135	1, 1, 7	3.136, 3.131, 3.131	222, −412, −151
4	2.983	3, 2	2.984, 2.975	142, −421
11	2.924	3, 12	2.924, 2.920	−333, −251
4	2.893	1, 2, 1	2.894, 2.888, 2.884	−114, −342, 232
2	2.821	1	2.820	−243
6	2.762	4, 0.5, 3	2.774, 2.757, 2.756	−423, −431, −432
1	2.689	1, 1	2.690, 2.684	−324, 312
3	2.647	1, 3	2.646, 2.645	−161, −343
5	2.609	7	2.609	−351
5	2.532	6	2.534	223
4	2.522	1, 2	2.526, 2.519	−334, −442
2	2.461	3	2.459	104
1	2.415	1, 1	2.416, 2.413	−521, −244
2	2.386	4	2.381	−353
1	2.335	1	2.333	−532
2	2.289	2, 1	2.289, 2.288	−451, −452
2	2.245	1	2.243	134
3	2.183	1, 3	2.184, 2.181	−542, 323
2	2.155	2	2.155	214
1	2.079	0.5, 2	2.080, 2.078	432, −461
1	2.021	0.5, 2	2.022, 2.017	180, 081
1	1.969	2	1.969	600
1	1.922	0.5, 0.5, 2	1.927, 1.921, 1.916	−416, 244, 304
1	1.898	2	1.899	−155
1	1.873	0.5	1.874	−126
1	1.865	1, 1	1.867, 1.863	281, 353
1	1.822	1, 0.5, 2	1.822, 1.821, 1.820	055, −644, 380
1	1.799	1	1.800	−265
2	1.791	1, 1, 0.5	1.794, 1.792, 1.788	−704, 551, 560
1	1.739	1	1.736	344
1	1.587	0.5, 1	1.583, 1.583	−1.10.2, 632
1	1.540	0.5, 2	1.540, 1.536	−185, 1.10.2
1	1.524	0.5	1.522	−3.10.2
1	1.465	0.5, 1	1.467, 1.462	−647, −518
1	1.373	1	1.372	821
1	1.355	0.5, 1	1.351, 1.351	672, −921

* Only reflections with $I_{calc} \geq 0.5$ are given;
** for the unit cell parameters calculated from single-crystal data.

mellizinkalite, flinteite, kainite, gypsum, sellaite and incompletely studied K-Pb-Cu chloride; hematite, tenorite and chalcocyanite are earlier, sublimate minerals.

Feodosiyite occurs as well-formed or, more commonly, crude, tabular or prismatic crystals up to $0.015 \times 0.04 \times 0.05$ mm^3, rarely up to $0.02 \times 0.1 \times 0.1$ mm^3. Thin polysynthetic twinning was observed under the microscope in some crystals. Crystal groups or crusts are up to 1 mm across (Fig. 1). Interrupted incrustations consisting of feodosiyite crystals (Fig. 2) up to 0.5×1 cm^2 in area and up to 0.1 mm thick overgrow basalt scoria.

Physical properties and optical characteristics

Feodosiyite is bright green, with light green streak. It is transparent and has vitreous lustre. The mineral is brittle. Its Mohs' hardness is *ca* 3. One direction of imperfect cleavage was observed under the microscope. The fracture is uneven. The density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.57(1) g cm^{-3}. The density calculated using the empirical formula is 2.563 g cm^{-3}.

Feodosiyite is optically biaxial (−), with $\alpha = 1.660(3)$, $\beta = 1.690(5)$, $\gamma = 1.718(5)$ (589 nm), $2V_{meas} = 90(5)°$ and $2V_{calc} = 86.5°$. Dispersion of the optical axes is very strong, $r > v$. Pleochroism is distinct: Z (grass green) > Y (light yellowish-green) > X (pale green with greyish hue).

Raman spectroscopy

The Raman spectrum of feodosiyite (Fig. 3) was recorded using an EnSpectr R532 spectrometer with a green laser (532 nm) at room temperature. The power of the laser beam on the sample was about 7 mW. The spectrum was processed using the EnSpectr expert mode program in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 lines cm^{-1} and a resolution equal to 5–8 cm^{-1}. The diameter of the focal spot on the sample was about 10 μm. Raman spectrum was acquired on a randomly oriented crystal.

The Raman bands are assigned according to NAKA-MOTO (1986). Bands in the range from 3500 to 3250 cm^{-1} correspond to O–H stretching vibrations. We assume that the strong, narrow band with maximum at 3386 cm^{-1} and the shoulder at 3461 cm^{-1} correspond to vibrations of hydroxyl groups whereas the broad band at 3310 cm^{-1} corresponds to vibrations of H_2O molecules. The relatively weak band at 1615 cm^{-1} corresponds to H–O–H bending vibrations of H_2O molecules. The bands with maxima at 898, 857 and 807 cm^{-1} are assigned to O–H libration (in other terms, $Cu^{2+}\cdots$O–H bending) modes. The band

Table 2. Crystal data, data collection information and structure refinement details.

Formula used for refinement / Idealized formula	$(Cu_{10.62}Mg_{0.38})Mg_2Cl_{18}(OH)_8 \times 16H_2O$ / $Cu_{11}Mg_2Cl_{18}(OH)_8 \times 16H_2O$
Formula weight	1795.07
Temperature, K	293(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/c$, 2
Unit cell dimensions, Å/°	$a = 12.9010(6)$ $b = 16.4193(5)$ $\beta = 113.691(6)$ $c = 11.9614(5)$
V, Å^3	2320.20(17)
Absorption coefficient μ, mm^{-1}	5.9
F_{000}	1749
Crystal size, mm^3	$0.03 \times 0.04 \times 0.06$
Diffractometer	Xcalibur S CCD
θ range for data collection, °	3.02–27.10
Index ranges	$-16 \le h \le 16, -21 \le k \le 21, -15 \le l \le 15$
Exposure time, sec.	120
Reflections collected	34420
Independent reflections	5112 ($R_{int} = 0.1286$)
Independent reflections with $I > 2\sigma(I)$	4028
Data reduction	CrysAlisPro, version 1.171.35.21 (AGILENT TECHNOLOGIES 2012)
Absorption correction	multi-scan [empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	310
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0867$, w$R2 = 0.1040$
R indices (all data)	$R1 = 0.1181$, w$R2 = 0.1119$
GoF	1.25
Largest diff. peak and hole, e/Å^3	0.83 (at 0.98 Å from Cu(1)) and -0.83

at 485 cm^{-1} corresponds to Cu^{2+}–O stretching vibrations whereas the bands at 396 and 325 cm^{-1} can be assigned to Cu^{2+}–O and/or Mg–O stretching modes. The bands with frequencies below 300 cm^{-1} probably correspond to lattice modes involving, in particular, Cu^{2+}–Cl vibrations.

Chemical data

Chemical data for feodosiyite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 5 μm beam diameter. The following standards were used: diopside (Mg), CuFeS$_2$ (Cu), and NaCl (Cl). H$_2$O was

not determined directly because of the paucity of pure material.

The average (5 spot analyses) chemical composition of feodosiyite (wt.%, ranges are in parentheses; H$_2$O calculated by total difference) is: MgO 5.39 (4.84–5.91), Cu 46.98 (45.46–49.29), Cl 35.42 (34.23–37.28), H$_2$O$_{calc}$ 20.21, $-$O = Cl -8.00, total 100.00. Contents of other elements with atomic numbers higher than carbon are below detection limits.

The empirical formula calculated on the basis of 42 atoms O+Cl *pfu* is: Cu$_{10.58}$Mg$_{2.40}$Cl$_{17.90}$(OH)$_{8.06}$ · 16.04H$_2$O. The idealized formula is Cu$_{11}$Mg$_2$Cl$_{18}$(OH)$_8$ · 16H$_2$O, which requires MgO 4.45, Cu 48.35, Cl 35.25, H$_2$O 19.91, $-$O = Cl -7.96, total 100.00 wt.%.

Feodosiyite slowly dissolves in H$_2$O at room temperature. In humid air the mineral is unstable and alters to a bluish friable aggregate of hydrous Cu and Mg chlorides after several months.
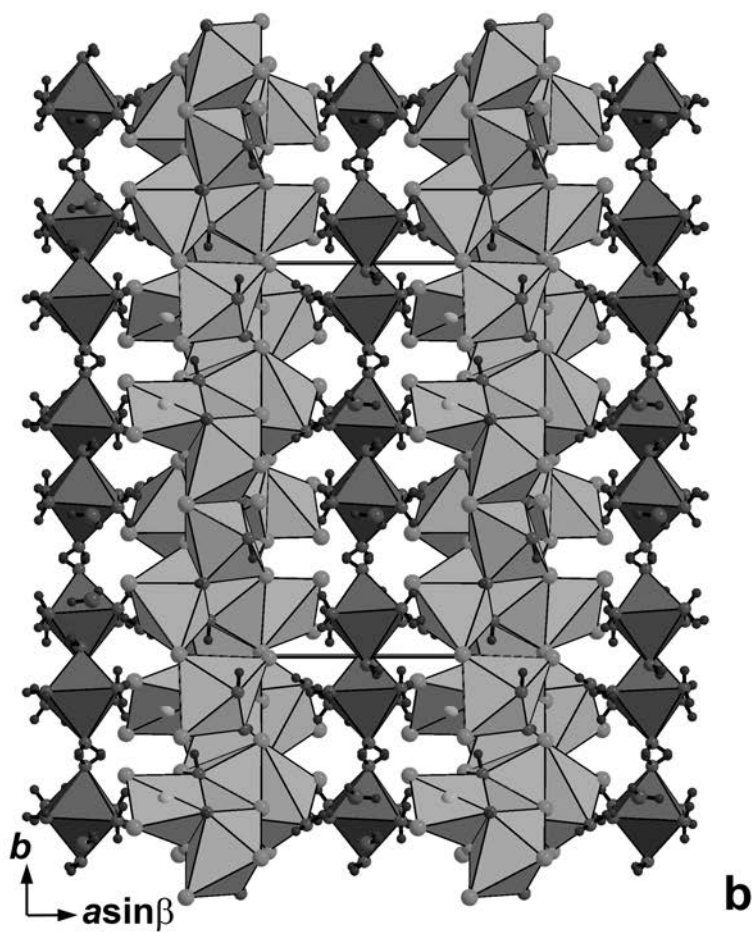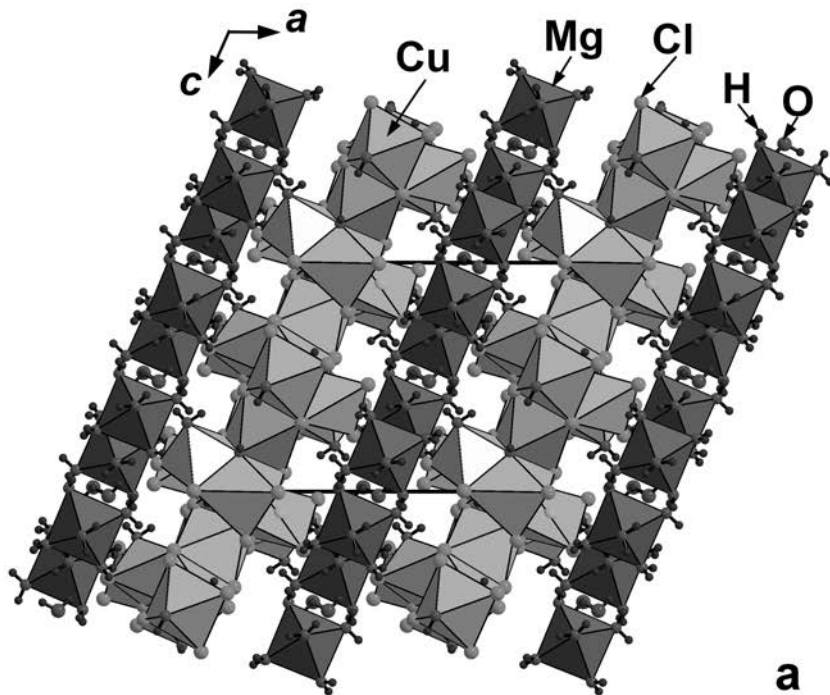
Fig. 4. The crystal structure of feodosiyite projected along the *b* (a) and *a* (b) axes. The unit cell is outlined.
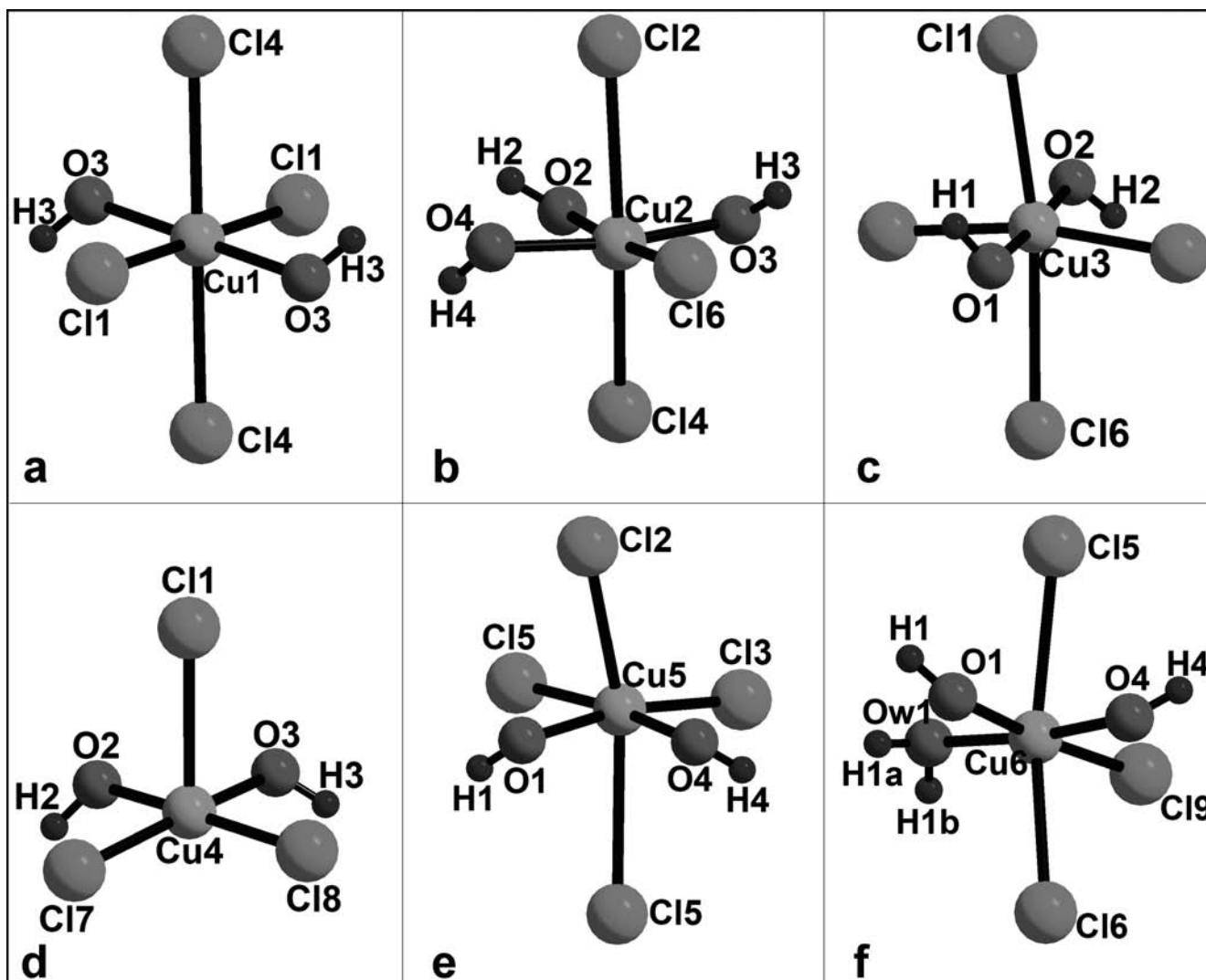
Fig. 5. The coordination environment of Cu^{2+} cations in the structure of feodosiyite.

X-ray crystallography

Powder X-ray diffraction data (Table 1) for feodosiyite were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry ($d = 127.4$ mm; Co$K\alpha$-radiation). The parameters of monoclinic unit cell refined from the powder data are: $a = 12.917(8)$, $b = 16.434(5)$, $c = 11.969(9)$ Å, $\beta = 113.71(5)°$ and $V = 2326(3)$ Å^3.

Single-crystal X-ray studies were carried out using an Xcalibur S CCD diffractometer. A full sphere of three-dimensional data was collected. Crystal data, data collection information and structure refinement details are given in Table 2. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined with the use of SHELX software package (SHELDRICK 2008) on the basis of 4028 independent reflections with $I > 2\sigma(I)$ to $R1(F) = 0.0867$. Coordinates and thermal displacement parameters of atoms and site occupancies are given in Tables 3 and 4, selected interatomic distances in Table 5, hydrogen-bond geometry in Table 6 and bond valence calculations in Table 7. Unfortunately, even the best of many tested crystals of feodosiyite was not too perfect that caused the relatively high value of $R1(F)$. However, the reasonable values of atomic displacement parameters and interatomic distances, as well as bond valence calculations and good agreement between the measured and calculated powder X-ray diffraction patterns show that the obtained structure model is correct.

Table 3. Atom coordinates and equivalent thermal displacement parameters (U_{eq}, in Å^2) and site occupancies (s.o.f.) for feodosiyite

Site	x	y	z	U_{eq}	s.o.f.
Cu(1)	0.0	0.5	0.5	0.0138(5)	Cu$_{0.97(1)}$Mg$_{0.03(1)}$
Cu(2)	−0.02132(9)	0.29385(6)	0.45926(9)	0.0127(3)	Cu$_{0.96(1)}$Mg$_{0.04(1)}$
Cu(3)	−0.01958(8)	0.64878(6)	0.26368(9)	0.0144(3)	Cu$_{0.97(1)}$Mg$_{0.03(1)}$
Cu(4)	0.20180(9)	0.36537(6)	0.60058(9)	0.0166(4)	Cu$_{0.97(1)}$Mg$_{0.03(1)}$
Cu(5)	−0.04489(9)	0.59933(6)	−0.00976(9)	0.0140(3)	Cu$_{0.96(4)}$Mg$_{0.04(1)}$
Cu(6)	0.18964(9)	0.63540(6)	0.15694(9)	0.0178(4)	Cu$_{0.97(1)}$Mg$_{0.03(1)}$
Mg	0.5017(3)	0.39998(17)	0.1577(3)	0.0228(7)	1
Cl(1)	0.13148(18)	0.48647(12)	0.69858(18)	0.0212(5)	1
Cl(2)	−0.14836(17)	0.70553(12)	0.08337(18)	0.0184(5)	1
Cl(3)	−0.12067(19)	0.60755(12)	−0.21444(18)	0.0228(5)	1
Cl(4)	0.13281(18)	0.61321(12)	0.44290(18)	0.0216(5)	1
Cl(5)	−0.15776(18)	0.49578(12)	−0.00339(19)	0.0203(5)	1
Cl(6)	−0.13366(19)	0.28436(12)	0.25673(19)	0.0253(5)	1
Cl(7)	0.34435(19)	0.30371(14)	0.7548(2)	0.0296(6)	1
Cl(8)	0.3154(2)	0.43591(15)	0.5327(2)	0.0341(6)	1
Cl(9)	0.33497(19)	0.68633(13)	0.1213(2)	0.0309(6)	1
Oh(1)	0.0498(5)	0.5912(3)	0.1692(5)	0.0151(13)	1
H(1)	0.055(7)	0.5412(14)	0.189(7)	0.018	1
Oh(2)	0.0879(4)	0.2997(3)	0.6356(5)	0.0137(12)	1
H(2)	0.103	0.248	0.653	0.016	1
Oh(3)	0.0597(5)	0.3967(3)	0.4592(5)	0.0145(13)	1
H(3)	0.065(7)	0.401(5)	0.391(4)	0.017	1
Oh(4)	−0.0719(5)	0.1857(3)	0.4881(5)	0.0161(13)	1
H(4)	−0.087(6)	0.185(5)	0.551(4)	0.019	1
Ow(1)	0.2927(6)	0.5712(4)	0.3008(5)	0.0298(16)	1
H(1a)	0.255(5)	0.555(5)	0.341(6)	0.036	1
H(1b)	0.350(4)	0.597(5)	0.350(5)	0.036	1
Ow(2)	0.3816(6)	0.1085(4)	0.7322(7)	0.0422(19)	1
H(2a)	0.346(6)	0.073(3)	0.755(9)	0.051	1
H(2b)	0.347(7)	0.154(2)	0.725(9)	0.051	1
Ow(3)	0.3735(6)	0.8791(4)	0.1694(6)	0.0441(19)	1
H(3a)	0.332(5)	0.839(3)	0.167(9)	0.053	1
H(3b)	0.332(5)	0.918(3)	0.128(8)	0.053	1
Ow(4)	0.4887(8)	0.2203(4)	0.6253(7)	0.050(2)	1
H(4a)	0.511(7)	0.246(5)	0.578(8)	0.061	1
H(4b)	0.434(6)	0.247(5)	0.630(9)	0.061	1
Ow(5)	0.3725(6)	0.5899(5)	−0.0941(7)	0.050(2)	1
H(5a)	0.371(7)	0.602(6)	−0.026(4)	0.060	1
H(5b)	0.305(3)	0.592(6)	−0.147(5)	0.060	1
Ow(6)	0.4960(7)	0.4785(4)	0.8073(6)	0.046(2)	1
H(6a)	0.462	0.454	0.849	0.055	1
H(6b)	0.454(7)	0.465(6)	0.735(3)	0.055	1
Ow(7)	0.5350(7)	0.3566(5)	0.5188(6)	0.055(2)	1
H(7a)	0.4636(16)	0.362(7)	0.483(7)	0.067	1
H(7b)	0.558(7)	0.334(6)	0.469(7)	0.067	1
Ow(8)	0.3757(6)	0.4192(4)	−0.0151(5)	0.0354(17)	1
H(8a)	0.356(8)	0.382(3)	−0.068(5)	0.042	1
H(8b)	0.374(8)	0.464(2)	−0.051(6)	0.042	1

All hydrogen atoms were found in the difference Fourier synthesis, O–H distances were restrained to 0.85(1) Å (H···H distances for H_2O molecules were restrained to 1.37(2) Å) and their temperature factor was set to $1.2U_{eq}$(O). Positions of two H atoms [H(2) and H(6a)] were fixed during the refinement to avoid their movement resulting in unrealistic interatomic distances with neighboring cations. The O–H distances are 0.87 and 0.89 Å, respectively.

Table 4. Anisotropic thermal displacement parameters (in $Å^2$) for feodosiyite.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0190(9)	0.0085(8)	0.0107(8)	−0.0002(6)	0.0025(7)	0.0026(6)
Cu(2)	0.0168(6)	0.0080(5)	0.0107(6)	0.0000(4)	0.0029(5)	−0.0021(4)
Cu(3)	0.0171(6)	0.0162(6)	0.0093(6)	−0.0002(4)	0.0046(5)	0.0049(4)
Cu(4)	0.0140(6)	0.0163(6)	0.0176(6)	0.0007(5)	0.0044(5)	−0.0002(4)
Cu(5)	0.0190(6)	0.0117(6)	0.0088(6)	0.0000(4)	0.0030(5)	−0.0019(4)
Cu(6)	0.0143(6)	0.0209(6)	0.0165(6)	0.0039(5)	0.0044(5)	0.0030(5)
Mg	0.0246(18)	0.0188(15)	0.0218(17)	0.0010(13)	0.0060(15)	−0.0005(13)
Cl(1)	0.0277(13)	0.0169(11)	0.0141(11)	−0.0018(9)	0.0033(10)	0.0026(9)
Cl(2)	0.0209(12)	0.0174(11)	0.0157(11)	0.0019(9)	0.0060(10)	0.0034(9)
Cl(3)	0.0310(14)	0.0227(11)	0.0133(11)	−0.0007(9)	0.0076(10)	−0.0038(10)
Cl(4)	0.0206(12)	0.0270(12)	0.0147(11)	0.0025(9)	0.0048(10)	0.0049(9)
Cl(5)	0.0282(13)	0.0138(10)	0.0224(12)	−0.0042(9)	0.0138(10)	−0.0042(9)
Cl(6)	0.0317(14)	0.0201(12)	0.0159(12)	0.0011(9)	0.0009(10)	−0.0030(10)
Cl(7)	0.0193(13)	0.0333(13)	0.0277(13)	−0.0007(11)	0.0005(11)	0.0059(10)
Cl(8)	0.0307(14)	0.0383(14)	0.0334(14)	0.0026(11)	0.0130(12)	−0.0078(11)
Cl(9)	0.0221(13)	0.0324(14)	0.0396(15)	−0.0054(11)	0.0140(12)	−0.0063(10)
Oh(1)	0.020(3)	0.009(3)	0.018(3)	−0.002(3)	0.009(3)	0.001(2)
Oh(2)	0.018(3)	0.011(3)	0.012(3)	0.000(2)	0.006(3)	−0.001(2)
Oh(3)	0.022(3)	0.008(3)	0.012(3)	−0.003(2)	0.005(3)	0.001(2)
Oh(4)	0.020(3)	0.017(3)	0.012(3)	0.001(3)	0.008(3)	−0.001(2)
Ow(1)	0.033(4)	0.041(4)	0.020(4)	0.007(3)	0.015(3)	−0.006(3)
Ow(2)	0.031(4)	0.050(5)	0.049(5)	0.001(4)	0.019(4)	−0.001(4)
Ow(3)	0.033(4)	0.050(5)	0.032(4)	0.004(4)	−0.004(4)	−0.013(4)
Ow(4)	0.086(7)	0.023(4)	0.052(5)	0.002(4)	0.037(5)	0.000(4)
Ow(5)	0.042(5)	0.073(6)	0.040(5)	−0.009(5)	0.023(4)	−0.014(5)
Ow(6)	0.060(6)	0.026(4)	0.042(5)	0.000(4)	0.010(4)	−0.009(4)
Ow(7)	0.058(6)	0.071(6)	0.039(5)	0.004(4)	0.021(5)	−0.010(5)
Ow(8)	0.051(5)	0.025(4)	0.024(4)	−0.001(3)	0.008(4)	−0.005(4)
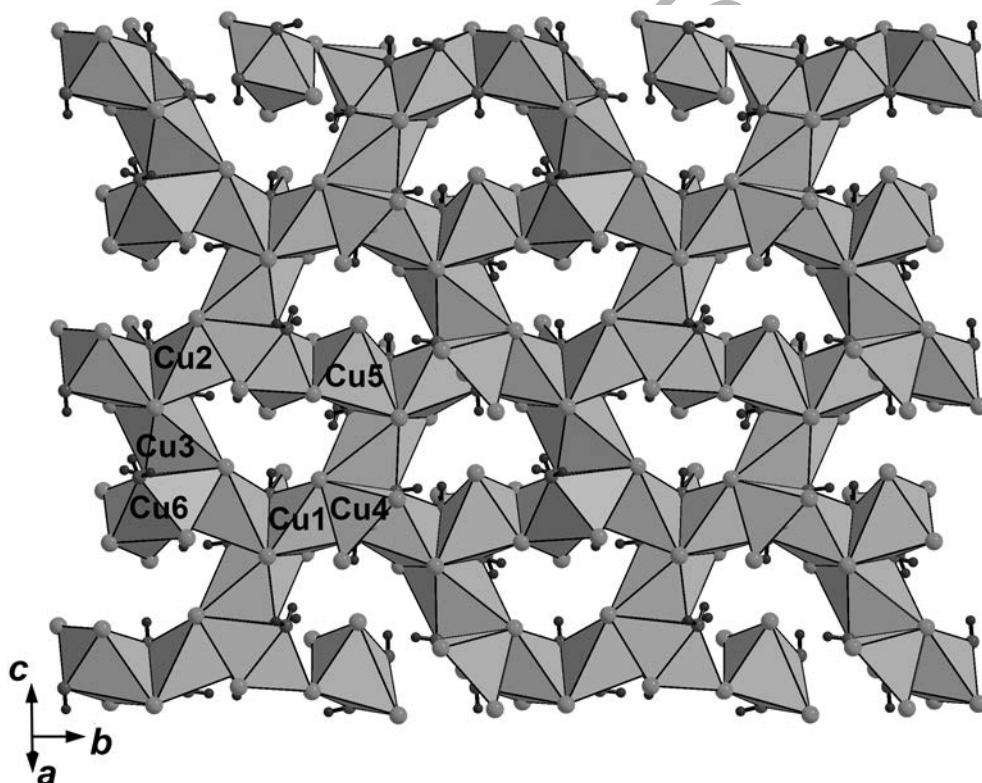
Fig. 6. The layer formed by Cu-centred polyhedra in the crystal structure of feodosiyite. For legend see Figure 4

Table 5. Selected interatomic distances (Å) in the structure of feodosiyite.

Cu(1)	– Oh(3)	2.003(5) × 2	Cu(5)	– Oh(1)	1.998(6)
	– Cl(1)	2.309(2) × 2		– Oh(4)	2.010(5)
	– Cl(4)	2.792(2) × 2		– Cl(3)	2.246(2)
Cu(2)	– Oh(4)	1.969(5)		– Cl(5)	2.260(2)
	– Oh(3)	1.986(5)		– Cl(2)	2.694(2)
	– Oh(2)	2.014(5)		– Cl(5)	2.995(2)
	– Cl(6)	2.274(2)	Cu(6)	– Oh(4)	1.971(5)
	– Cl(4)	2.668(2)		– Ow(1)	2.000(7)
	– Cl(2)	2.838(2)		– Oh(1)	2.004(5)
Cu(3)	– Oh(1)	1.945(5)		– Cl(9)	2.245(2)
	– Oh(2)	1.948(5)		– Cl(5)	2.752(2)
	– Cl(2)	2.324(2)		– Cl(6)	2.858(2)
	– Cl(4)	2.327(2)	Mg	– Ow(4)	2.006(7)
	– Cl(1)	2.783(2)		– Ow(6)	2.037(7)
	– Cl(6)	3.052(2)		– Ow(5)	2.058(7)
Cu(4)	– Oh(3)	1.998(6)		– Ow(3)	2.076(7)
	– Oh(2)	1.999(5)		– Ow(8)	2.077(7)
	– Cl(7)	2.255(2)		– Ow(2)	2.079(7)
	– Cl(8)	2.260(2)			
	– Cl(1)	2.647(2)			

Table 6. Hydrogen-bond geometry (Å,°) in the structure of feodosiyite.

$D – H\cdots A$	H$\cdots A$	$D\cdots A$	$\angle(D – H\cdots A)$
Oh(1) – H(1)···Cl3	2.56(3)	3.373(5)	160(7)
Oh(2) – H(2)···Cl3	2.410(2)	3.271(5)	170.0(3)
Oh(3) – H(3)···Cl3	2.49(2)	3.324(5)	167(7)
Oh(4) – H(4)···Cl6	2.808(19)	3.640(5)	168(7)
Ow(1) – H(1a)···Cl(4)	2.55(6) 2.87(7)	3.231(6) 3.473(6)	139(7)
Ow(1) – H(1a)···Cl(8)			130(7)
Ow(1) – H(1b)···Ow(7)	1.84(2)	2.674(9)	168(7)
Ow(2) – H(2a)···Cl(3)	2.81(7)	3.287(7)	117(6)
Ow(2) – H(2b)···Cl(7)	2.50(4)	3.268(8)	152(8)
Ow(3) – H(3a)···Cl(9)	2.57(6)	3.220(8)	135(8)
Ow(3) – H(3b)···Cl(8)	2.63(4) 2.69(7)	3.387(7) 3.200(7)	149(7)
Ow(3) – H(3b)···Cl(4)			120(7)
Ow(4) – H(4a)···Ow(7)	2.01(5)	2.757(11)	146(8)
Ow(4) – H(4b)···Cl(7)	2.42(5)	3.173(8)	148(9)
Ow(5) – H(5a)···Cl(9)	2.43(4)	3.223(7)	156(9)
Ow(5) – H(5b)···Cl(1)	2.85(7) 2.89(7)	3.536(8) 3.567(8)	139(9)
Ow(5) – H(5b)···Cl(6)			138(8)
Ow(6) – H(6a)···Cl(7)	2.875(2)	3.386(7)	118.4(4)
Ow(6) – H(6b)···Cl(8)	2.404(18)	3.248(7)	173(10)
Ow(7) – H(7a)···Cl(8)	2.52(6)	3.182(9)	135(7)
Ow(7) – H(7b)···Ow(3)	2.29(8)	2.955(11)	136(10)
Ow(8) – H(8a)···Cl(7)	2.43(3) 2.98(8)	3.231(6) 3.396(7)	159(7)
Ow(8) – H(8a)···Cl(2)			112(7)
Ow(8) – H(8b)···Ow(5)	2.13(2)	2.953(11)	164(7)

Table 7. Bond valence calculations for feodosiyite

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	Cu(6)	Mg	Σ	H-bonding	Σ
Cl(1)	0.43 ×2↓		0.12	0.17				0.72	+0.06 (Ow(5))	0.78
Cl(2)		0.10	0.42		0.15			0.67	+0.04 (Ow(8))	0.71
Cl(3)					0.51			0.51	+0.10 (Oh(1)) +0.13(Oh(2)) + 0.11 (Oh(3)) +0.06 (Ow(2))	0.91
Cl(4)	0.12 ×2↓	0.16	0.41					0.69	+0.10(Ow(1)) +0.08(Ow(3))	0.87
Cl(5)					0.50 0.07	0.13		0.70		0.70
Cl(6)		0.48	0.06			0.10		0.64	+0.06 (Oh(4)) +0.05 (Ow(5))	0.75
Cl(7)				0.50				0.50	+0.11 (Ow(2)) +0.13 (Ow(4)) +0.05 (Ow(6)) +0.13 (Ow(8))	0.92
Cl(8)				0.50				0.50	+0.06 (Ow(1)) +0.09 (Ow(3)) +0.11 (Ow(7)) +0.13 (Ow(6))	0.89
Cl(9)						0.52		0.52	+0.10 (Cl(9)) +0.13 (Ow(5))	0.75
Oh(1) = OH			0.49		0.42	0.42		1.33	−0.10 (Cl(3))	1.23
Oh(2) = OH		0.40	0.48	0.42				1.30	−0.13 (Cl(3))	1.17
Oh(3) = OH	0.42 ×2↓	0.44		0.42				1.28	−0.11 (Cl(3))	1.17
Oh(4) = OH		0.46			0.41	0.45		1.32	−0.06 (Cl(6))	1.26
Ow(1) = H_2O						0.42		0.42	−0.10 (Cl(4)) −0.06(Cl(8)) −0.24(Ow(7))	0.02
Ow(2) = H_2O							0.35	0.35	−0.06 (Cl(3)) −0.11 (Cl(7))	0.18
Ow(3) = H_2O							0.36	0.36	−0.10 (Cl(9)) −0.09 (Cl(8)) −0.08(Cl(4)) +0.14 (Ow(7))	0.23
Ow(4) = H_2O							0.43	0.43	−0.20 (Ow(7)) −0.13 (Cl(7))	0.10
Ow(5) = H_2O							0.37	0.37	−0.13 (Cl(9)) −0.06 (Cl(1)) −0.05 (Cl(6)) +0.14 (Ow(8))	0.27
Ow(6) = H_2O							0.39	0.39	−0.05 (Cl(7)) −0.13 (Cl(8))	0.21
Ow(7) = H_2O							0.00	0.00	+0.24(Ow(1)) +0.20 (Ow(4)) −0.11 (Cl(8)) −0.14 (Ow(3))	0.19
Ow(8) = H_2O							0.35	0.35	−0.14 (Ow(5)) −0.13 (Cl(7)) −0.04 (Cl(2))	0.04
Σ	1.94	2.04	1.98	2.01	2.06	2.04	2.25			

For Cu(1–6) positions bond valences were calculated for the sites fully occupied by Cu atoms. Bond-valence parameters were taken from (BRESE & O'KEEFFE 1991) and for H-bonding from (FERRARIS & IVALDI 1988, MALCHEREK & SCHLÜTER 2007).

Crystal structure: description and discussion

The crystal structure of feodosiyite is unique. It consists of the layers of Cu^{2+}-centred polyhedra and isolated Mg-centred octahedra located in the interlayer space (Fig. 4). Cu^{2+} cations occupy six crystallographically non-equivalent sites (Table 3). Coordination polyhedra of all Cu cations except Cu(4) are distorted octahedra: [(2(OH)+2Cl) + 2Cl] for Cu(1,3,5) cations, [(3(OH)+Cl) + 2Cl] for Cu(2) and [(2(OH)+H_2O+Cl)+2Cl] for Cu(6). Cu(4) cations are five-coordinated [(2(OH)+2Cl)+Cl] and occupy distorted tetragonal pyramids with two short Cu-OH bonds [1.996(5) and 1.998(6) Å], two short Cu-Cl bonds [2.255(2) and 2.260(2) Å] and one long Cu-Cl bond [2.647(2) Å]. The coordination environment of Cu^{2+} cations in the structure of feodosiyite is shown on Figure 5. The geometry of mixed-ligand $Cu^{2+}\Phi_6$ octahedra (F = O^{2-}, OH^-, H_2O^0 and Cl^-) was examined by BURNS & HAWTHORNE (1995) who showed that mixed-ligand $Cu^{2+}\Phi_6$ octahedra are characterized by Jahn-Teller distortion (JAHN & TELLER 1937) and although a holosymmetric coordination is impossible due to the participation of different types of ligands, a pseudo-holosymmetric octahedral geometry would occur and involves a near-degenerate electronic state. Thus either an elongation [(4 + 2)-distortion] or a compression [(2 + 4)-distortion] of the ligand geometry will serve to remove the near-degenerate electronic state and result in a net stabilization of the octahedron (BURNS & HAWTHORNE 1995). Later a review on mixed-ligand CuO_mCl_n coordination geometries was given by KRIVOVICHEV et al. (2012). Six-fold coordination of Cu^{2+} cations with three Cl anions found for Cu(2) and Cu(6) polyhedra in the structure of feodosiyite is very rare in copper compounds; it was earlier reported in three synthetic compounds, namely Cu(OH)Cl (an analogue of belloite) (IITAKA et al. 1961; EFFENBERGER 1984), $K_2Cu_5Cl_8(OH)_4 \times 2H_2O$ (an analogue of avdoninite) (KAHLENBERG 2004), and $SrCu_2(SeO_3)_2Cl_2$ (BERDONOSOV et al. 2009), and four minerals, all from the Tolbachik fumaroles: burnsite $KCdCu_7O_2(SeO_3)_2Cl_9$ (BURNS et al. 2002; KRIVOVICHEV et al. 2002b), avdoninite $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$ (PEKOV et al. 2016a), allochalcoselite $Cu^+Cu^{2+}_5PbO_2(SeO_3)_2Cl_5$ (KRIVOVICHEV et al. 2006), and ilinskite $NaCu_5O_2(SeO_3)_2Cl_3$ (KRIVOVICHEV et al. 2012); for allochalcoselite and ilinskite the six-fold coordination of Cu^{2+} cations is completed by strongly elongated Cu-Cl bonds included in the coordination sphere. Note the configurations of Cu(1)-, Cu(3)- and Cu(5)-centred octahedra in the structure of feodosiyite are different: in the first two polyhedra, two (OH) and two Cl ligands forming a distorted square base are in a *trans* arrangement

while in the latter they are in a *cis* arrangement (Fig. 5). The first case is more typical; such arrangement was reported in the structures of chlorothionite $K_2Cu(SO_4)Cl_2$ (GIACOVAZZO et al. 1976) and synthetic analogues of eriochalcite $CuCl_2 \times 2H_2O$ (ENGBERG 1970; BROWNSTEIN et al. 1989) and melanothallite Cu_2OCl_2 (ARPE & MÜLLER-BUSCHBAUM 1977; KRIVOVICHEV et al. 2002a). $Cu^{2+}\Phi_6$ octahedra in the structure of feodosiyite are [4 + 2]-distorted, with two significantly elongated apical Cu-Cl bonds. All Cu positions are characterized by minor Mg admixture: $Cu_{0.96-0.97}Mg_{0.04-0.}03$ (Table 3) that is in agreement with electron microprobe data. Cu-centred polyhedra share edges to form layers coplanar to the *bc* plane (Fig. 6). Isolated from one another almost regular $Mg(H_2O)_6$ octahedra, linked with the layers of Cu-centred polyhedra by the system of H-bonds, occur in the interlayer space, as well as separate H_2O molecules [Ow(7), H(7a) and H(7b) atoms belong to them: Table 3] involved only in hydrogen bonding system (Table 6).

Thus, Cu^{2+} and Mg cations are ordered in feodosiyite which is related to the character of their coordination polyhedra. Mg-centred octahedra in the new mineral are much more regular in comparison with Cu^{2+} polyhedra that demonstrate a significant Jahn-Teller distortion. The same ordering was reported for earlier known natural Cu-Mg hydroxychlorides represented by three modifications of $Cu_3Mg(OH)_6Cl_2$: haydeeite (MALCHEREK & SCHLÜTER 2007), paratacamite-(Mg) (KAMPF et al. 2013) and tondiite (MALCHEREK et al. 2014). This also is typical for the majority of other Cu-Mg oxysalts (TURCHKOVA et al. 2016, and references therein; PEKOV et al. 2017).

Acknowledgements

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