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Chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4{\cdot}H_2O$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia

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ABSTRACT

A new mineral chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4{\cdot}H_2O$ was found in two active fumaroles, Glavnaya Tenoritovaya and Pyatno, at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. Chrysothallite seems to be a product of the interactions involving high-temperature sublimate minerals, fumarolic gas and atmospheric water vapour at temperatures not higher than 150ºC. It is associated with belloite, avdoninite, chlorothionite, sanguite, eriochalcite, mitscherlichite, sylvite, carnallite and kainite at Glavnaya Tenoritovaya and with belloite, avdoninite, chlorothionite, eriochalcite, atacamite, halite, kröhnkite, natrochalcite, gypsum and antlerite at Pyatno. The mineral forms equant-to-thick tabular crystals up to 0.05 mm, typically combined in clusters or crusts up to 1 mm across. Crystal forms are: {001}, {100}, {110}, {101} and {102}. Chrysothallite is transparent, bright golden-yellow to light yellow in finely crystalline aggregates. The lustre is vitreous. The mineral is brittle. Cleavage was not observed, the fracture is uneven. D_{meas} = 2.95(2), D_{calc} = 2.97 g cm^{-3}. Chrysothallite is optically uniaxial (+), ω = 1.720(5), ε = 1.732(5). The Raman spectrum is given. The chemical composition (wt.%, electron-microprobe data, H_2O calculated based on the crystal structure data) is: K 15.92, Cu 24.56, Zn 1.38, Tl 13.28, Cl 40.32, H_2O(calc.) 3.49, total 98.95. The empirical formula, calculated on the basis of 17 Cl + 5 O a.p.f.u., is: $K_{6.09}(Cu_{5.78}Zn_{0.32})_{\Sigma 6.10}Tl_{0.97}Cl_{17}[(OH)_{3.80}O_{0.20}]{\cdot}H_2O$. Chrysothallite is tetragonal, *I*4/*mmm*, a = 11.3689(7), c = 26.207(2) Å, V = 3387.3(4) Å^3, Z = 4. The strongest reflections of the powder X-ray pattern [d,Å(I)(hkl)] are: 13.20(44)(002); 6.88(100)(112); 5.16(30)(202, 114); 4.027(25)(220); 3.471(28)(206), 3.153(30)(314), 3.075(47)(305), 2.771(38)(316). The crystal structure (solved from single-crystal X-ray diffraction data, R = 0.0898) is unique. Its basic structural unit is a (001) layer of edge-sharing distorted $CuCl_4(OH)_2$ octahedra. Two Tl^{3+} cations occupy the centre of isolated $TlCl_6$ and $TlCl_4(H_2O)_2$ octahedra connected to each other and to the Cu polyhedral layers *via* KCl_6 and KCl_9 polyhedra. The name reflects the bright golden-yellow colour of the mineral (from the Greek χρυσός, gold) and the presence of thallium. Chrysothallite is the second known mineral with species-defining trivalent thallium.

Keywords: chrysothallite, new mineral, chloride, trivalent thallium, crystal structure, fumarole, Tolbachik volcano, Kamchatka.

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Introduction

Fifty four minerals with thallium as a species-defining element are known at present. The majority of them (41 species) are sulfides with strongly predominant As- and/or Sb-bearing sulfosalts. The other 13 include three selenides, five sulfates, one oxide and four chlorides. The latter are represented by three minerals of univalent thallium discovered in sublimates of active fumaroles at the La Fossa crater, Vulcano island, Aeolian archipelago, Italy: lafossaite $Tl^{+}(Cl,Br)$ (Roberts *et al*., 2006), hephaistosite $Tl^{+}Pb_2Cl_5$ (Campostrini *et al*., 2008) and steropesite $Tl^{+}BiCl_3$ (Demartin *et al*., 2009) and by the new species chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4{\cdot}H_2O$ described in the present paper. Chrysothallite is the second mineral, after avicennite Tl_2O_3, with species-defining trivalent thallium.

The name chrysothallite (Russian Cyrillic: хризоталлит) reflects the bright golden-yellow colour of the mineral (from the Greek χρυσός, gold) and the presence of thallium as a species-defining constituent. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2013−008, Pekov *et al*., 2013). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the catalogue number is 94129.

Occurrence and general appearance

Specimens with the new mineral were collected by us during fieldwork at the Tolbachik volcano in July 2012. Chrysothallite was found in the material from two active fumaroles, Glavnaya Tenoritovaya ("Major Tenorite") and Pyatno ("Spot"), at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55º41′N 160º14′E, 1200 m asl). This scoria cone, formed in 1975, is a monogenetic volcano (~300 m high and ~0.1 km^3 in volume) situated 18 km south-southwest of the active volcano Ploskiy Tolbachik (Fedotov and Markhinin, 1983).

The Glavnaya Tenoritovaya and Pyatno fumaroles are located in the western wall of a big contraction fracture cross-cutting the top of the scoria cone in the near-meridional direction. The main sublimate minerals in the inner, hottest zones of both fumaroles (350−360ºC, from our measurements performed in 2013) are sulfates (euchlorine, dolerophanite, chalcocyanite, anglesite, krasheninnikovite and anhydrite), hematite and tenorite. The chloride mineralization occurs in outer, moderately hot parts of the fumaroles. The temperature measured in July 2013 within the area richest in chloride (with chrysothallite) in the northern part of the Glavnaya Tenoritovaya fumarole was 110ºC. In Glavnaya Tenoritovaya, the new mineral is closely associated with belloite, avdoninite, chlorothionite, sanguite $KCuCl_3$ (IMA 2013-002), eriochalcite, mitscherlichite, sylvite, carnallite and kainite. In Pyatno, chrysothallite was found in association with belloite, avdoninite, chlorothionite, eriochalcite, atacamite, halite, kröhnkite, natrochalcite, gypsum and antlerite. Hematite and tenorite are earlier sublimate minerals associated with chrysothallite in both fumaroles.

Chrysothallite forms equant-to-thick tabular crystals commonly up to 0.02 mm, rarely up to 0.05 mm in size. The crystals belong to the symmetry class 4/*mmm* and are typically complicated, showing combinations of the following faces: pinacoid {001}, tetragonal prisms {100} and {110} and tetragonal dipyramids {101} and {102} (Figs 1*a*−*d* and 2). Some crystals are simpler in shape, up to pseudocubic (Fig. 1*d*−*e*).

Chrysothallite crystals are usually combined in clusters up to 0.2 mm across or in thin crusts (Figs 1 and 3) up to 1 mm across. They occur on the surface of basalt scoria (Fig. 3*a*) or on polycomponent chloride or sulfate-chloride incrustations (Figs 1*a* and 3*b*). Areas up to 1 mm × 5 mm 'sprinkled' with the numerous crystal clusters or small crusts of chrysothallite (Fig. 3*b*) were found in the Glavnaya Tenoritovaya fumarole.

Physical properties and optical data

Chrysothallite is transparent, bright golden-yellow in larger crystals to light yellow in finely crystalline aggregates. The streak is yellow. The lustre is vitreous. The mineral is brittle. The Mohs' hardness was not determined exactly; it is estimated to be <3. Cleavage or parting were not observed, the fracture is uneven. Density measured by flotation in heavy liquids (CH_2I_2 + C_3H_7NO) is 2.95(2) g cm^{-3}, the calculated density is 2.97 g cm^{-3} (for the empirical formula).

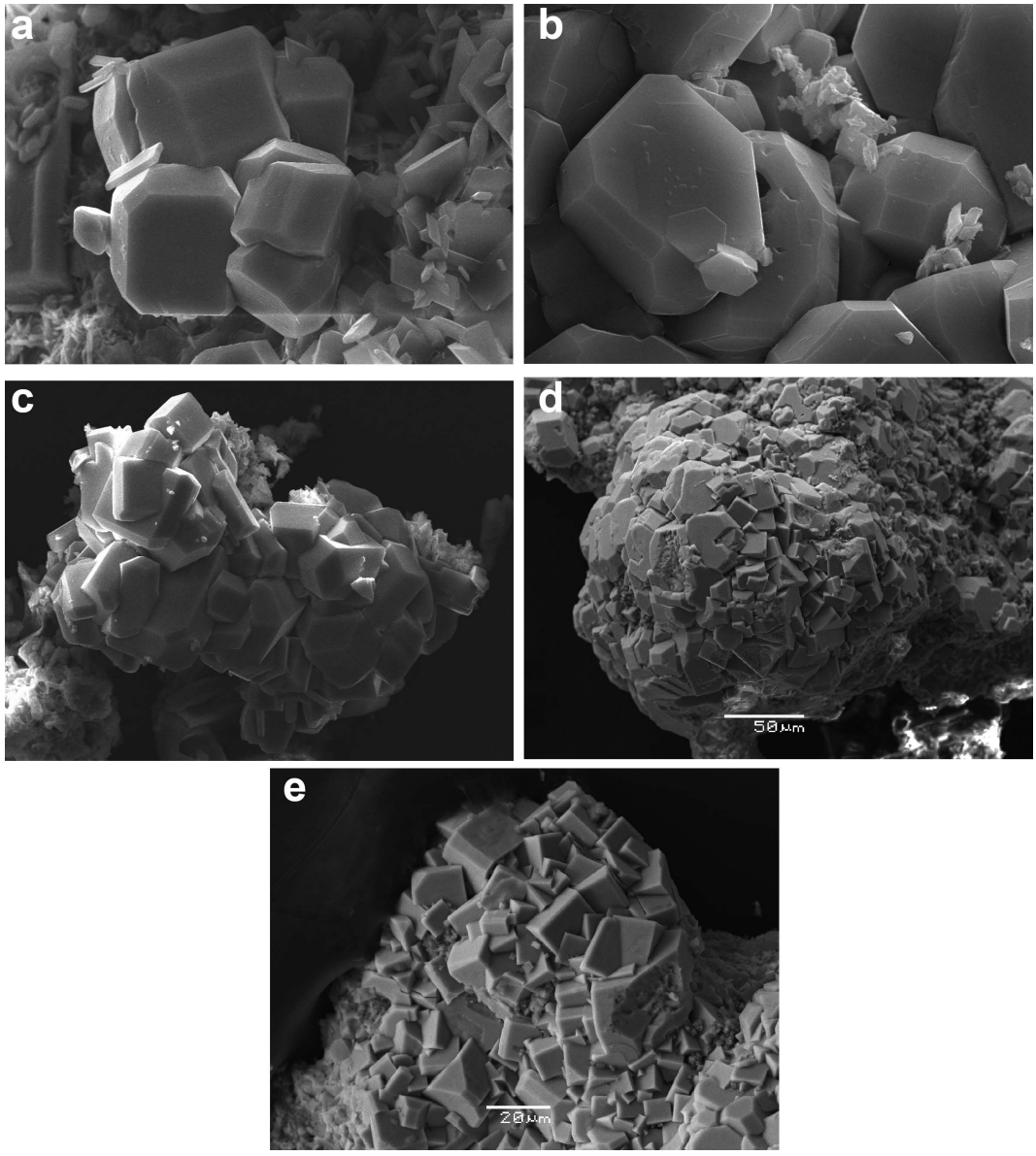

FIG. 1. Scanning electron microscopy secondary electron images of chrysothallite crystal clusters and crusts: (*a*–*b*) from the Pyatno fumarole ((*a*) on a chlorothionite crystal crust; (b) with overgrowing small hexagonal lamellar crystals of belloite); and (*c*–*e*) from the Glavnaya Tenoritovaya fumarole. Fields of view: (*a*) 110, (*b*) 40, (*c*) 240 μm across.

Chrysothallite is optically uniaxial (+), ω = 1.720(5), ε = 1.732(5) (589 nm). In transmitted light the mineral is yellow with a very weak pleochroism in yellow tones; the absorption scheme is $O > E$. Elongation is positive.

Raman spectroscopy

The Raman spectrum of chrysothallite (Fig. 4) was obtained using a HORIBA Scientific XploRA System (Jobin Yvon) with a green laser (532 nm) at room temperature. The power of the laser beam

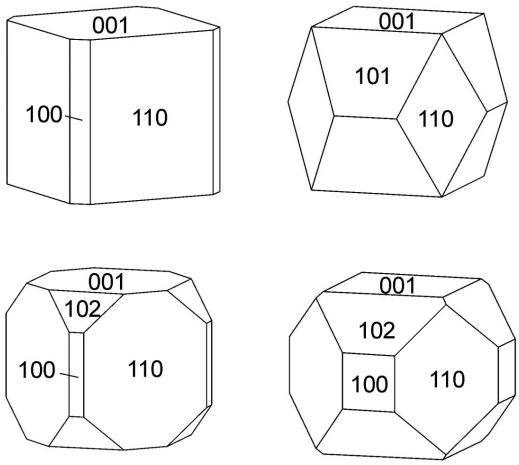

FIG. 2. Idealized crystals of chrysothallite.

at the sample was ~0.1 mW. The spectrum was processed using the *LabSpec 5* program from 100 to 3800 cm^{-1} with a diffraction grating 1800 mm^{-1}. The diameter of the focal spot on the sample was ~15 μm. The backscattered Raman signal was collected with a 50× objective; signal acquisition time for a single scan of the spectral range was 200 s and the signal was averaged over five scans. The spectrum was obtained for a randomly oriented crystal.

The intense band with a maximum at 3443 cm^{-1} corresponds to O–H stretching vibrations, and the relatively weak, broad band at 1580 cm^{-1} can be assigned to bending vibrations of H_2O molecules. Bands with maxima at 944 and 902 cm^{-1} correspond to O–H libration (in other terms, $Cu^{2+}\cdots$O–H bending) modes. The band with a maximum at 465 cm^{-1} corresponds to Cu^{2+}–O stretching vibrations, as well as, probably, the band with a maximum at 320 cm^{-1}. Several intense, narrow bands with frequencies below 300 cm^{-1} correspond to lattice modes involving Cu^{2+}–Cl, Tl^{3+}–Cl and K–Cl vibrations. An absence of distinct absorption bands in the regions 1000–1500 and 1700–3000 cm^{-1} indicates the absence of isolated H^+ cations and groups with C–O, C–H, N–O and B–O bonds in chrysothallite.

Chemical data

Chemical data were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA and a beam diameter of 5 μm. The following standards were used: microcline (K), $CuFeS_2$ (Cu), ZnSe (Zn), $TlAsS_2$ (Tl) and NaCl (Cl). H_2O was not analysed because of the paucity of pure material. The H_2O content was calculated based on the crystal structure data (see below).

The average (four spot analyses) chemical composition of chrysothallite (wt.%, ranges are in parentheses) is: K 15.92 (15.33–16.39), Cu 24.56 (24.17–24.91), Zn 1.38 (1.03–1.68), Tl

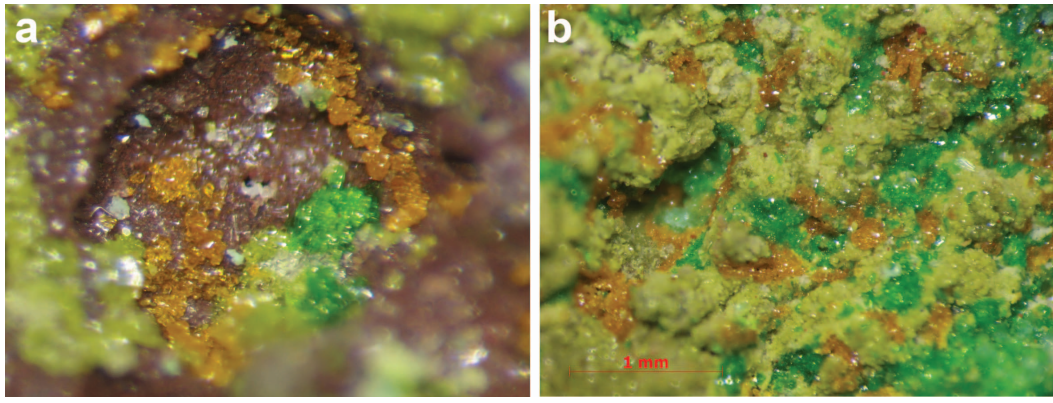

FIG. 3. Crystal clusters and small crusts of golden-yellow chrysothallite: (*a*) with bright green avdoninite, olive-green belloite, pale bluish chlorothionite and aqua-transparent, colourless halite on basalt scoria from the Pyatno fumarole; (*b*) with bright green avdoninite and minor pale bluish chlorothionite on a light olive-green belloite crust from the Glavnaya Tenoritovaya fumarole.

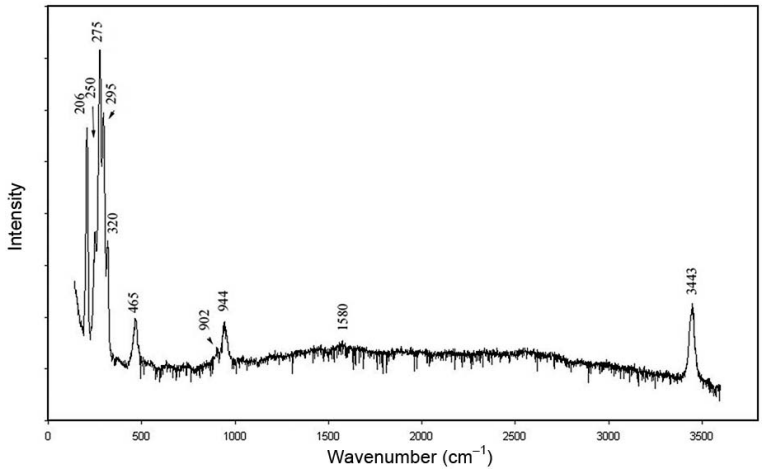

FIG. 4. Raman spectrum of chrysothallite.

13.28 (12.98–13.66), Cl 40.32 (39.92–40.69), H_2O(calc.) 3.49, total 98.95. The amounts of other elements with atomic numbers larger than carbon are below detection limits.

The empirical formula of chrysothallite, calculated on the basis of 17 Cl + 5 O atoms per formula unit (with H_2O = 1 per formula unit and the OH^-/O^{2-} ratio calculated by charge balance), is: $K_{6.09}(Cu_{5.78}Zn_{0.32})_{\Sigma 6.10}Tl_{0.97}Cl_{17}[(OH)_{3.80}O_{0.20}]\cdot H_2O$. The simplified formula is $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4\cdot H_2O$, which requires K 15.88, Cu 25.82, Tl 13.84, Cl 50.88, H_2O 3.66, total 100 wt.%.

Chrysothallite hydrolyses at room temperature. On being placed in water it turns dull and pale green over a 1 min period and then decomposes further slowly.

X-ray crystallography and crystal structure

Powder X-ray diffraction (XRD) data (Table 1) for chrysothallite were collected using a STOE IPDS II diffractometer equipped with an Image Plate area detector, using the Gandolfi method (Mo$K\alpha$-radiation; detector-to-sample distance: 200 mm). Unit-cell parameters refined from the powder data are: a = 11.366(6), c = 26.22(2) Å, V = 3387(6) Å^3.

Single-crystal X-ray studies were carried out using an Xcalibur S CCD diffractometer. A full sphere of reciprocal space was measured. The data were corrected for Lorentz factor and polarization effects. Crystal data, data-collection information and structure-refinement details are given in Table 2. An absorption correction was applied according to the shape of the crystal. The structure model was obtained by direct methods and refined with the use of the *SHELX-97* software package (Sheldrick, 2008) on the basis of 1005 independent reflections with $I > 2\sigma(I)$ to R = 0.0898. At the last stages of the refinement a peak which was included in the structure as an H atom of the OH group was found in the difference-Fourier map. The O–H distance was softly constrained to 0.90 Å. Atom coordinates and displacement parameters are given in Table 3, selected interatomic distances in Table 4 and bond-valence calculations in Table 5. Unfortunately, even the best of many tested crystals of chrysothallite was not perfect, which caused the relatively large value of R. However, the reasonable values of atomic displacement parameters (Table 3), interatomic distances (Table 4), bond-valence calculations (Table 5) and good agreement between the measured and calculated powder XRD patterns (Table 1) show that our structure model is correct.

The crystal structure of chrysothallite (Fig. 5) is unique. Its basic structural unit is a (001) layer of edge-sharing distorted $CuCl_4(OH)_2$ octahedra with four short [two Cu–Cl and two Cu–(OH)] distances and two elongated Cu–Cl distances (Table 4; Fig. 6). Two crystallographically inequivalent Tl^{3+} cations occupy the centre of isolated $Tl(1)Cl_6$ and $Tl(2)Cl_4(H_2O)_2$ octahedra (Fig. 5). These are connected to each other and to the layers formed by Cu-centred polyhedra *via* distorted $K(3)Cl_6$ octahedra and $K(1)Cl_9$ and $K(2)Cl_9$ polyhedra (Fig. 5*c*).

TABLE 1. Powder X-ray diffraction data for chrysothallite.

I_{obs}	d_{obs} (Å)	I_{calc}*	d_{calc} (Å)**	*h k l*
44	13.20	35	13.104	002
15	10.47	4	10.430	101
9	8.14	8	8.039	110
100	6.88	100	6.852	112
18	5.69	14	5.684	200
30	5.16	22, 18	5.215, 5.079	202, 114
26	4.027	25	4.020	220
8	3.849	4, 2	3.843, 3.838	222, 116
7	3.610	4	3.595	310
28	3.471	31	3.463	206
7	3.270	7	3.276	008
30	3.153	27	3.152	314
47	3.075	47	3.071	305
8	2.985	3, 2	3.015, 2.966	217, 323
14	2.844	11, 1	2.842, 2.838	400, 208
38	2.771	15, 23, 19	2.778, 2.776, 2.742	402, 316, 411
14	2.624	8, 4, 10	2.625, 2.621, 2.607	332, 0.0.10, 404
17	2.536	8, 4, 13	2.542, 2.539, 2.527	420, 228, 219
8	2.428	3, 9	2.440, 2.421	415, 318
22	2.383	24, 7	2.382, 2.370	406, 424
3	2.267	3	2.265	431
12	2.196	1, 10	2.200, 2.197	503, 426
8	2.178	6	2.184	0.0.12
8	2.105	6, 2	2.111, 2.107	514, 1.1.12
7	2.086	4, 3	2.086, 2.074	505, 338
15	2.006	11, 4, 7	2.010, 2.008, 2.002	440, 428, 419
9	1.926	6, 4	1.927, 1.921	4.0.10, 444
12	1.895	14	1.895	600
22	1.876	3, 2, 26	1.875, 1.874, 1.874	602, 2.1.13, 3.3.10
6	1.825	2, 2, 2	1.828, 1.826, 1.825	613, 446, 4.2.10
5	1.804	6	1.803	4.1.11
5	1.787	2	1.781	622
6	1.777	1, 4	1.778, 1.771	2.0.14, 541
2	1.736	1	1.734	624
6	1.700	2, 4, 2	1.698, 1.698, 1.697	3.2.13, 5.1.10, 2.2.14
4	1.661	4, 2	1.660, 1.657	3.1.14, 4.2.12
4	1.651	1, 3	1.652, 1.645	2.1.15, 5.0.11
3	1.608	4	1.608	710
2	1.587	3	1.587	3.0.15
4	1.561	3, 1, 1, 1, 2	1.565, 1.564, 1.563, 1.561, 1.559	642, 5.3.10, 4.0.14, 554, 721
2	1.529	2, 1	1.533, 1.528	644, 1.0.17
3	1.519	2, 2	1.517, 1.516	2.2.16, 549
4	1.510	2, 1, 1	1.509, 1.508, 1.507	716, 4.3.13, 4.2.14
7	1.483	2, 5, 6	1.483, 1.483, 1.479	732, 646, 4.4.12
3	1.459	3	1.456	734
5	1.417	1, 6	1.419, 1.413	4.0.16, 736
2	1.396	1	1.398	3.3.16
4	1.370	5	1.370	5.5.10
3	1.359	2, 2	1.362, 1.358	745, 738
1	1.333	2	1.331	2.1.19
3	1.297	1, 2, 2, 1	1.297, 1.296, 1.296, 1.295	6.2.14, 4.0.18, 754, 7.1.12
2	1.276	1	1.276	4.3.17
2	1.271	1, 1	1.271, 1.270	840, 4.4.16
4	1.222	1, 3	1.221, 1.220	763, 846

Table 1 (*contd.*)

I_{obs}	d_{obs} (Å)	I_{calc}*	d_{calc} (Å)**	*h k l*
3	1.215	1, 1	1.216, 1.214	6.3.15, 8.1.11
3	1.208	1, 1	1.211, 1.207	6.2.16, 916
2	1.192	2	1.191	8.0.12
2	1.169	1, 1, 1	1.174, 1.172, 1.167	855, 918, 7.3.14
2	1.136	1	1.137	860
2	1.092	2	1.090	9.3.10

* For the calculated powder XRD pattern only reflections with $I_{calc} \geqslant 1$ are given. ** Calculated for unit-cell parameters obtained from single-crystal data.

Discussion

One of the remarkable features of chrysothallite is the presence of species-defining Tl^{3+}, a very rare occurrence in minerals. Convincing evidence for the trivalent state of thallium in the new mineral is found in the Tl–Cl distances in both Tl(1)- and Tl(2)-centred octahedra (Table 4; Fig. 7) and the sums of bond valences for Tl cations (Table 5). In chrysothallite, the Tl–Cl distances vary in the range 2.26–2.82 Å, whereas the K–Cl distances vary between 3.07 and 3.46 Å. The distances Tl^{3+}–Cl^{-} in well-studied synthetic chlorides are as follows (Å): $KTl^{3+}Cl_4$ 2.42 (Glaser, 1980), $Tl^{+}Tl^{3+}Cl_4$ 2.42 (Thiele and Rink, 1975), $Tl^{+}_3Tl^{3+}Cl_6$ 2.51–2.73 (Boehme *et al*., 1980), $K_3Tl^{3+}Cl_6{\cdot}2H_2O$ 2.55–2.56 (Hoard and Goldstein, 1935), $K_2Tl^{3+}Cl_5{\cdot}2H_2O$ 2.48–2.79 (Thiele and Grunwald, 1983). The distances Tl^{+}–C^{-} in the same chlorides are as follows (Å; for references see above): $Tl^{+}Tl^{3+}Cl_4$ 3.27–3.29, $Tl^{+}_3Tl^{3+}Cl_6$ 3.03–3.83. In $Tl^{+}Cl$ the distances Tl^{+}–Cl^{-} vary between 3.15 and 3.72 Å (Ungelenk, 1962). The distances K^{+}–Cl^{-} in the same compounds are as follows (Å; for references

TABLE 2. Crystal data, data-collection information and structure-refinement details for chrysothallite.

Idealized formula	$K_6Cu_6Tl^{3+}Cl_{17}(OH)_4{\cdot}H_2O$
Formula weight	1508.91
Temperature (K)	293(2)
Radiation (wavelength, Å)	Mo$K\alpha$ (0.71073)
Crystal system, space group; *Z*	Tetragonal, *I*4/*mmm*; 4
Unit-cell dimensions (Å)	a = 11.3689(7)
	c = 26.207(2)
V (Å^3)	3387.3(4)
Absorption coefficient μ, (mm^{-1})	10.530
F_{000}	2816
Crystal size (mm)	0.04 × 0.05 × 0.06
Diffractometer	Xcalibur S CCD
θ range for data collection (º)	2.53–26.35
Index ranges	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-32 \leqslant l \leqslant 32$
Reflections collected	26,347
Independent reflections	1048 (R_{int} = 0.1724)
Independent reflections with $I > 2\sigma(I)$	1005
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	76
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0898, wR_2 = 0.1445
R indices (all data)	R_1 = 0.0946, wR_2 = 0.1460
Gof	1.480
Largest diff. peak and hole (e/Å^3)	1.916 and −1.545

TABLE 3. Atom coordinates, equivalent isotropic displacement parameters (U_{eq}, Å^2), site multiplicities (Q) and site occupancy factors (s.o.f.) for chrysothallite.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}	*Q*	s.o.f.
Cu(1)	0	½	0.65620(10)	0.0170(7)	8	1
Cu(2)	0.14638(12)	0.64638(11)	¾	0.0166(5)	16	1
Tl(1)	0	0	½	0.0194(8)	2	1*
K(1)	0.2104(3)	0.2104(3)	0.59487(17)	0.0389(11)	16	1
K(2)	0	0	0.7207(3)	0.0226(17)	4	1
K(3)	0	½	½	0.069(4)	4	1
Cl(1)	0.2298(7)	0	½	0.040(3)	8	1*
Cl(2)	0	0	0.5941(3)	0.033(2)	4	1
Cl(3)	0.1494(4)	½	0.59848(16)	0.0322(11)	16	1
Cl(4)	0	0.2589(4)	0.67703(16)	0.0231(9)	16	1
Cl(5)	0.3219(3)	0.3219(3)	0.70693(16)	0.0190(9)	16	1
'*Tl(2)*'**	½	½	½		2	1
'*Cl(6)*'**	0.3446	0.3446	½		8	1
Tl(2)	0.4560(5)	0.4560(5)	0.5302(3)	0.062(2)	16	0.125
Cl(6)	0.3758(17)	0.3758(17)	½	0.099(9)	8	0.50
Cl(6′)	0.3135(16)	0.3135(16)	½	0.084(7)	8	0.50
O*w*	½	½	0.6158(15)	0.066(10)	4	1
O	0	0.3769(9)	0.7889(4)	0.011(2)	16	1
H	0	0.313(8)	0.809(5)	0.013***	16	1

* Site occupancy factors for Tl(1) and Cl(1) sites were refined and gave the values 0.884(11) and 0.95(3), respectively. These values are fixed at 1.00 for the idealized structure model presented here.
** Positions of the Tl(2) cation and the Cl(6) anion bound with it, are disordered about the 2*a* Wyckoff site. Data on the 'idealized' positions of these atoms (given for clarity, in Fig. 5) are written in italics and quote marks. The real situation for Tl(2) and Cl(6) is shown in Fig. 7: The Tl(2) cation 'leaves' the 2*a* site '*Tl(2)*' and occupies one 16*m* site *Tl*(2); the '*Cl(6)*' anion position is in fact split into two sites *Cl*(6) and *Cl*(6′) with s.o.f. of 0.5 for each. This results in significant distortion of the Tl(2)-centred octahedron. Tables 4 and 5 contain data for the idealized model which involves only the positions '*Tl(2)*' and '*Cl(6)*'.
*** U_{iso}.

TABLE 4. Selected interatomic distances (Å) in the structure of chrysothallite.

Cu(1)−O	2.007(10) × 2	K(2)−Cl(4)	3.158(5) × 4
−Cl(3)	2.274(5) × 2	−Cl(2)	3.319(11)
−Cl(4)	2.795(4) × 2	−Cl(5)	3.434(6) × 4
Cu(2)−O	1.970(5) × 2	K(3)−Cl(1)	3.072(7) × 2
−Cl(5)	2.321(3) × 2	−Cl(3)	3.090(5) × 4
−Cl(4)	2.754(3) × 2		
		'*Tl(2)*'−'*Cl(6)*'	2.499 × 4*
Tl(1)−Cl(2)	2.466(7) × 2	−O*w*	3.035 × 2*
−Cl(1)	2.612(7) × 4		
		O−H	0.899(10)
K(1)−Cl(4)	3.265(5) × 2		
−Cl(3)	3.366(3) × 2		
−Cl(2)	3.382(5)		
−Cl(5)	3.441(6)		
−Cl(1)	3.457(4) × 2		
−'*Cl(6)*'	3.293*		

Only the positions '*Tl(2)*' and '*Cl(6)*' are presented (see footnote in Table 3).

TABLE 5. Bond-valence calculations for chrysothallite.

	Cu(1)	Cu(2)	K(1)	K(2)	K(3)	Tl(1)	'*Tl(2)*'*	Σ
Cl(1)			0.08 $^{\downarrow\times2\ \rightarrow\times4}$		0.22 $^{\downarrow\times2}$	0.45 $^{\downarrow\times4}$		0.99
Cl(2)			0.10 $^{\rightarrow\times4}$	0.11		0.67 $^{\downarrow\times2}$	1.18	
Cl(3)	0.48 $^{\downarrow\times2}$		0.10 $^{\downarrow\times2\ \rightarrow\times2}$		0.21 $^{\downarrow\times4}$			0.89
Cl(4)	0.12 $^{\downarrow\times2}$	0.13 $^{\downarrow\times2\ \rightarrow\times2}$	0.13 $^{\downarrow\times2\ \rightarrow\times2}$	0.18 $^{\downarrow\times4}$				0.82
Cl(5)		0.42 $^{\downarrow\times2\ \rightarrow\times2}$	0.08	0.08 $^{\downarrow\times4}$				1.00
'*Cl(6)*'*			0.12 $^{\rightarrow\times2}$				0.62 $^{\downarrow\times4}$	0.86
O = OH	0.41 $^{\downarrow\times2}$	0.45 $^{\downarrow\times2\ \rightarrow\times2}$						1.31
O*w* = H_2O							0.06 $^{\downarrow\times2}$	0.06
Σ	2.02	2.00	0.92	1.15	1.28	3.14	2.60**	

Bond-valence parameters were taken from Brese and O'Keeffe (1991). H bonding was not considered. Possible H bonds could slightly increase the value of bond-valence sums of Cl(3) and Cl(5).

* The idealized model which involves only the positions '*Tl(2)*' and '*Cl(6)*' (see Footnote in Table 3).

** We assume that the sum 2.60 for '*Tl(2)*' could be increased in this idealized model if the splitting absence leads to the O*w* shift and, thus, the '*Tl(2)*'−O*w* distances become shorter.

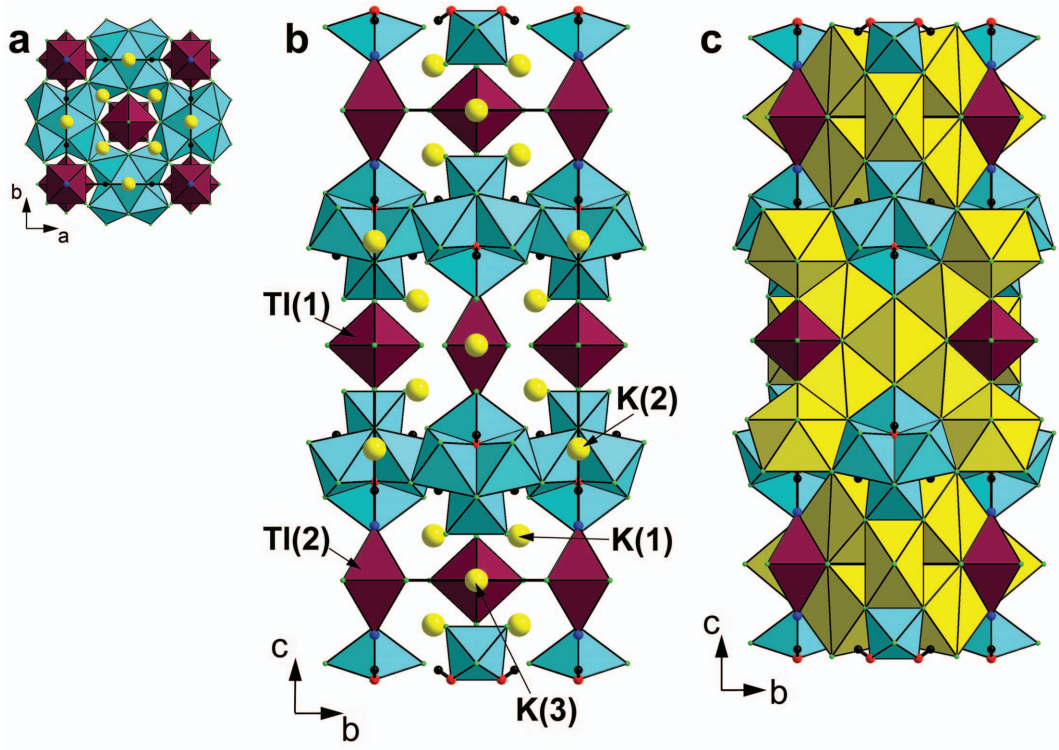

FIG. 5. The crystal structure of chrysothallite: (*a*) *ab* projection, (*b*) and (*c*) *bc* projection. Cu-centred polyhedra are turquoise-coloured, Cl atoms are green spheres, O atoms of OH groups are red spheres, H atoms of OH groups are black spheres and positions of O atoms belonging to H_2O molecules are dark blue spheres. K atoms are presented as yellow spheres in (*a*) and (*b*) whereas K-centred polyhedra (yellow) are shown in (*c*). The unit cell is outlined in (*a*) and (*b*).

see above): $KTl^{3+}Cl_4$ 3.19–3.26, $K_3Tl^{3+}Cl_6{\cdot}2H_2O$ 3.16–3.50, $K_2Tl^{3+}Cl_5{\cdot}2H_2O$ 3.15–3.67; this is in the same range as the Tl^{+}–Cl^{-} distances.

Thus, there is no doubt that the thallium in chrysothallite is Tl^{3+}. This is a consequence of strongly oxidizing conditions in mineral-forming systems related to the fumaroles of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. The fumarolic gases here are enriched by oxygen (Meniaylov *et al*., 1980; Zelenski *et al*., 2012) and elements with varying valences in minerals show only their high valence states, such as Fe^{3+}, As^{5+}, V^{5+}, S^{6+} and Mo^{6+}. Note that three new sulfate minerals with species-defining Tl^{+} were described recently from altered fumarolic deposits of the First scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption: markhininite $Tl^{+}Bi(SO_4)_2$, karpovite $Tl^{+}_2VO(SO_4)_2(H_2O)$ and evdokimovite $Tl^{+}_4(VO)_3(SO_4)_5(H_2O)_5$ (Siidra *et al*., 2014*a*,*b*,*c*). Minerals in the First scoria cone have the univalent form of Tl because the fumaroles in this location have, in general, less oxidizing conditions than fumaroles in the Second scoria cone.

The trivalent state of thallium is the cause of the Tl-K ordering in chrysothallite: it is the first mineral with Tl and K located in different sites and both these cations thus become species-defining.

In inner, hotter parts of the Tolbachik fumaroles, where the temperatures are greater than 180–200ºC (typically 350–430ºC, as our data show), only hydrogen-free minerals occur. Chrysothallite, which contains OH groups and H_2O molecules, is associated with other hydrous minerals, such as belloite CuCl(OH), atacamite $Cu_2Cl(OH)_3$, avdoninite $K_2Cu_5Cl_8(OH)_4{\cdot}2H_2O$, eriochalcite $CuCl_2{\cdot}2H_2O$, mitscherlichite $K_2CuCl_4{\cdot}2H_2O$, carnallite $KMgCl_3{\cdot}6H_2O$, natrochalcite $NaCu_2(SO_4)_2[(OH)(H_2O)]$, kröhnkite

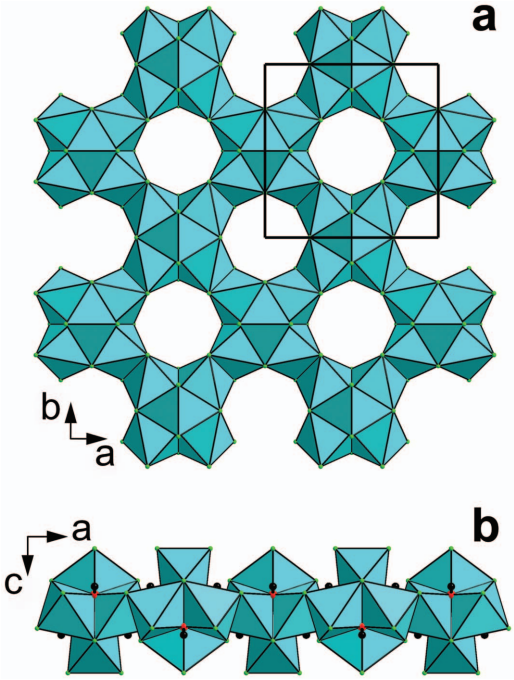

FIG. 6. The layer formed by Cu-centred polyhedra in chrysothallite: (*a*) *ab* projection, (*b*) *ac* projection. For legend see Fig. 5. The unit cell is outlined in (*a*).

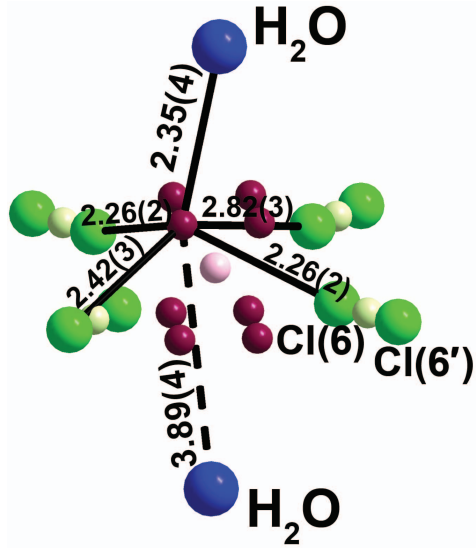

FIG. 7. Tl(2) cations (purple spheres) bound with O atoms of H_2O molecules, Cl(6) and Cl(6′) anions. Pink and pale greenish spheres mark, respectively, the '*Tl(2)*' and '*Cl(6)*' positions in the idealized model (see Table 3). Bond lengths are given in Å.

$Na_2Cu(SO_4)_2{\cdot}2H_2O$ and antlerite $Cu_3(SO_4)(OH)_4$. This demonstrates that chrysothallite was probably formed, not as the result of direct deposition from a gaseous phase (note that gases are sufficiently 'dry' in the fumaroles of the Second scoria cone, containing no more than 1% H_2O: Zelenski *et al*., 2012), but as a product of the interactions probably involving earlier, high-temperature sublimate minerals, HCl-bearing fumarolic gas and atmospheric water vapour at relatively low temperatures, presumably not >150ºC. In other words, the origin of chrysothallite can be characterized as a result of the combination of fumarolic and supergene processes. The presence of Tl^{3+} in chrysothallite is a strong indicator that mineral-forming conditions remain strongly oxidizing from high- to relatively low-temperature stages of the evolution of this fumarole system.

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