

# Chrysothallite $K_6Cu_6Ti^{3+}Cl_{17}(OH)_4 \cdot H_2O$ , a new mineral species from the Tolbachik volcano, Kamchatka, Russia

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## ABSTRACT

A new mineral chrysothallite  $K_6Cu_6Ti^{3+}Cl_{17}(OH)_4 \cdot H_2O$  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 150°C. 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.  $D_{\text{meas}} = 2.95(2)$ ,  $D_{\text{calc}} = 2.97 \text{ g cm}^{-3}$ . Chrysothallite is optically uniaxial (+),  $\omega = 1.720(5)$ ,  $\epsilon = 1.732(5)$ . 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, Ti 13.28, Cl 40.32,  $H_2O(\text{calc.})$  3.49, total 98.95. The empirical formula, calculated on the basis of 17 Cl + 5 O a.p.f.u., is:  $K_{6.09}(Cu_{5.78}Zn_{0.32})_{\Sigma 6.10}Ti_{0.97}Cl_{17}[(OH)_{3.80}O_{0.20}] \cdot H_2O$ . Chrysothallite is tetragonal,  $I4/mmm$ ,  $a = 11.3689(7)$ ,  $c = 26.207(2) \text{ \AA}$ ,  $V = 3387.3(4) \text{ \AA}^3$ ,  $Z = 4$ . The strongest reflections of the powder X-ray pattern [ $d, \text{\AA}(I)(hkl)$ ] 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  $Ti^{3+}$  cations occupy the centre of isolated  $TiCl_6$  and  $TiCl_4(H_2O)_2$  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 (55°41'N 160°14'E, 1200 m asl). This scoria cone, formed in 1975, is a monogenetic volcano (~300 m high and ~0.1 km<sup>3</sup> 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 (350–360°C, from our measurements performed in 2013) are sulfates (euchlorine, dolerophanite, chalcocyanite, angle-site, krashennikovite 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 110°C. 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 dipyrramids {101} and {102} (Figs 1a–d and 2). Some crystals are simpler in shape, up to pseudocubic (Fig. 1d–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. 3a) or on polycomponent chloride or sulfate-chloride incrustations (Figs 1a and 3b). Areas up to 1 mm × 5 mm ‘sprinkled’ with the numerous crystal clusters or small crusts of chrysothallite (Fig. 3b) 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<sup>-3</sup>, the calculated density is 2.97 g cm<sup>-3</sup> (for the empirical formula).

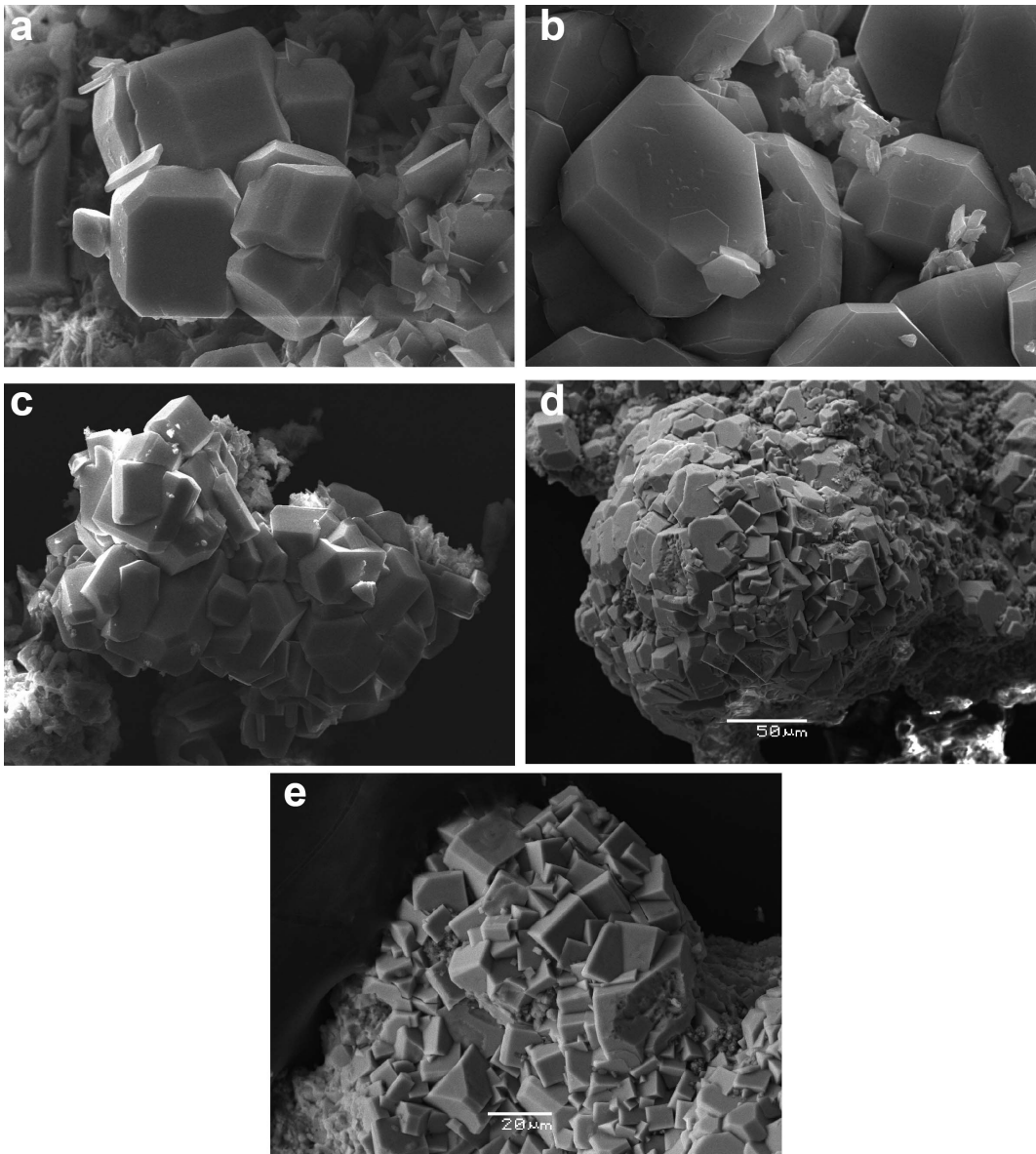


FIG. 1. Scanning electron microscopy secondary electron images of chrysothallite crystal clusters and crusts: (a–b) from the Pyatno fumarole ((a) on a chlorothionite crystal crust; (b) with overgrowing small hexagonal lamellar crystals of belloite); and (c–e) from the Glavnaya Tenoritovaya fumarole.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

Chrysothallite is optically uniaxial (+),  $\omega = 1.720(5)$ ,  $\varepsilon = 1.732(5)$  (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

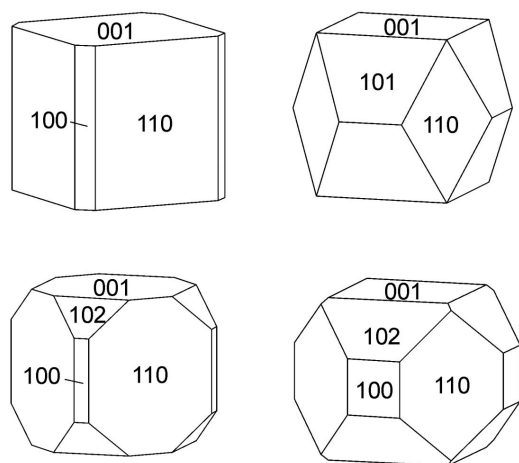


FIG. 2. Idealized crystals of chrysothallite.

at the sample was  $\sim 0.1$  mW. The spectrum was processed using the *LabSpec 5* program from 100 to  $3800\text{ cm}^{-1}$  with a diffraction grating  $1800\text{ mm}^{-1}$ . The diameter of the focal spot on the sample was  $\sim 15\text{ }\mu\text{m}$ . The backscattered Raman signal was collected with a  $50\times$  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  $3443\text{ cm}^{-1}$  corresponds to O–H stretching vibrations, and the relatively weak, broad band at  $1580\text{ cm}^{-1}$  can be assigned to bending vibrations

of  $\text{H}_2\text{O}$  molecules. Bands with maxima at  $944$  and  $902\text{ cm}^{-1}$  correspond to O–H libration (in other terms,  $\text{Cu}^{2+}\cdots\text{O}-\text{H}$  bending) modes. The band with a maximum at  $465\text{ cm}^{-1}$  corresponds to  $\text{Cu}^{2+}-\text{O}$  stretching vibrations, as well as, probably, the band with a maximum at  $320\text{ cm}^{-1}$ . Several intense, narrow bands with frequencies below  $300\text{ cm}^{-1}$  correspond to lattice modes involving  $\text{Cu}^{2+}-\text{Cl}$ ,  $\text{Ti}^{3+}-\text{Cl}$  and  $\text{K}-\text{Cl}$  vibrations. An absence of distinct absorption bands in the regions  $1000-1500$  and  $1700-3000\text{ cm}^{-1}$  indicates the absence of isolated  $\text{H}^+$  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  $5\text{ }\mu\text{m}$ . The following standards were used: microcline (K),  $\text{CuFeS}_2$  (Cu),  $\text{ZnSe}$  (Zn),  $\text{TiAsS}_2$  (Ti) and  $\text{NaCl}$  (Cl).  $\text{H}_2\text{O}$  was not analysed because of the paucity of pure material. The  $\text{H}_2\text{O}$  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), Ti

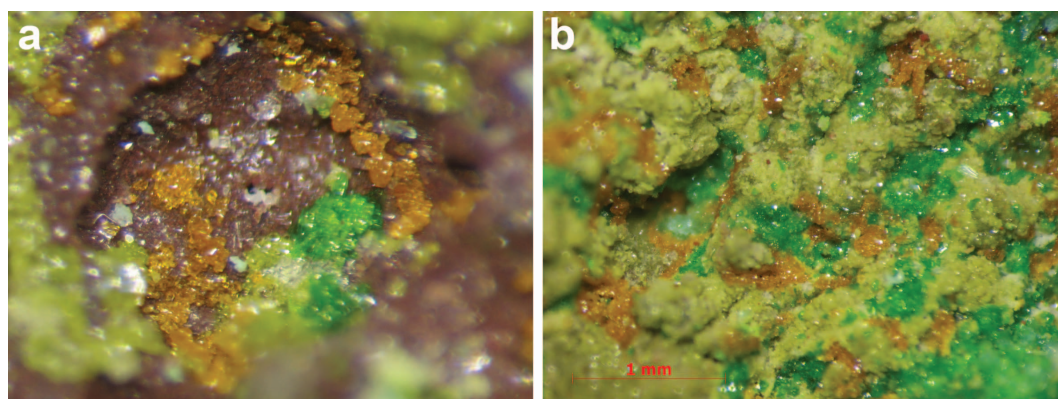


FIG. 3. Crystal clusters and small crusts of golden-yellow chrysothallite: (a) with bright green avdoninite, olive-green belloite, pale bluish chlorothionite and aqua-transparent, colourless halite on basalt scoria from the Pyatno fumarole; (b) with bright green avdoninite and minor pale bluish chlorothionite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



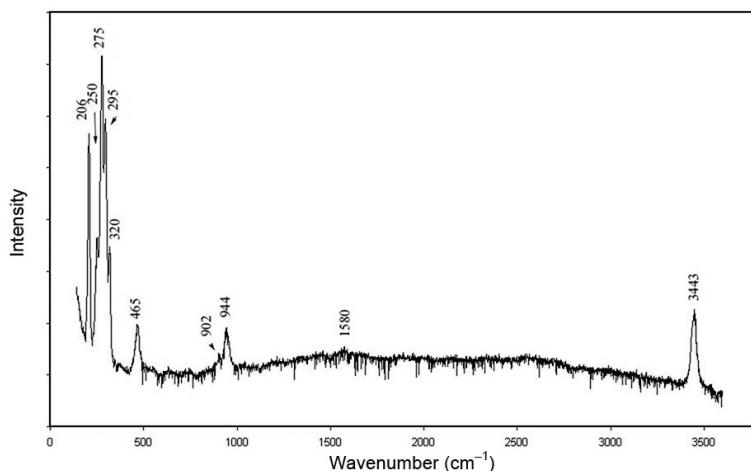


FIG. 4. Raman spectrum of chrysothallite.

13.28 (12.98–13.66), Cl 40.32 (39.92–40.69), H<sub>2</sub>O(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<sub>2</sub>O = 1 per formula unit and the OH<sup>-</sup>/O<sup>2-</sup> ratio calculated by charge balance), is: K<sub>6.09</sub>(Cu<sub>5.78</sub>Zn<sub>0.32</sub>)Σ<sub>6.10</sub>Tl<sub>0.97</sub>Cl<sub>17</sub>[(OH)<sub>3.80</sub>O<sub>0.20</sub>].H<sub>2</sub>O. The simplified formula is K<sub>6</sub>Cu<sub>6</sub>Tl<sup>3+</sup>Cl<sub>17</sub>(OH)<sub>4</sub>.H<sub>2</sub>O, which requires K 15.88, Cu 25.82, Tl 13.84, Cl 50.88, H<sub>2</sub>O 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 (MoK $\alpha$ -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<sup>3</sup>.

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<sub>4</sub>(OH)<sub>2</sub> 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<sup>3+</sup> cations occupy the centre of isolated Tl(1)Cl<sub>6</sub> and Tl(2)Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra (Fig. 5). These are connected to each other and to the layers formed by Cu-centred polyhedra *via* distorted K(3)Cl<sub>6</sub> octahedra and K(1)Cl<sub>9</sub> and K(2)Cl<sub>9</sub> polyhedra (Fig. 5c).

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

| $I_{\text{obs}}$ | $d_{\text{obs}}$ (Å) | $I_{\text{calc}}^*$ | $d_{\text{calc}}$ (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                      |

CHRYSOTHALLITE, A NEW MINERAL

Table 1 (contd.)

| $I_{\text{obs}}$ | $d_{\text{obs}}$ (Å) | $I_{\text{calc}}^*$ | $d_{\text{calc}}$ (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, 9.16     |
| 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  $I_{\text{calc}} \geq 1$  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  $\text{Tl}^{3+}$ , 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  $\text{Tl}^{3+}\text{--Cl}^-$  in well-studied synthetic chlorides are

as follows (Å):  $\text{KTl}^{3+}\text{Cl}_4$  2.42 (Glaser, 1980),  $\text{Tl}^+\text{Tl}^{3+}\text{Cl}_4$  2.42 (Thiele and Rink, 1975),  $\text{Tl}_3^+\text{Tl}^{3+}\text{Cl}_6$  2.51–2.73 (Boehme *et al.*, 1980),  $\text{K}_3\text{Tl}^{3+}\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  2.55–2.56 (Hoard and Goldstein, 1935),  $\text{K}_2\text{Tl}^{3+}\text{Cl}_5 \cdot 2\text{H}_2\text{O}$  2.48–2.79 (Thiele and Grunwald, 1983). The distances  $\text{Tl}^+\text{--Cl}^-$  in the same chlorides are as follows (Å; for references see above):  $\text{Tl}^+\text{Tl}^{3+}\text{Cl}_4$  3.27–3.29,  $\text{Tl}_3^+\text{Tl}^{3+}\text{Cl}_6$  3.03–3.83. In  $\text{Tl}^+\text{Cl}$  the distances  $\text{Tl}^+\text{--Cl}^-$  vary between 3.15 and 3.72 Å (Ungelenk, 1962). The distances  $\text{K}^+\text{--Cl}^-$  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                                  | $\text{K}_6\text{Cu}_6\text{Tl}^{3+}\text{Cl}_{17}(\text{OH})_4 \cdot \text{H}_2\text{O}$ |
| Formula weight                                     | 1508.91   |
| Temperature (K)                                    | 293(2)  |
| Radiation (wavelength, Å)                          | $\text{MoK}\alpha$ (0.71073)  |
| Crystal system, space group; Z                     | Tetragonal, $I4/mmm$ ; 4  |
| Unit-cell dimensions (Å)                           | $a = 11.3689(7)$<br>$c = 26.207(2)$   |
| $V$ (Å <sup>3</sup> )                              | 3387.3(4)   |
| Absorption coefficient $\mu$ , (mm <sup>-1</sup> ) | 10.530  |
| $F_{000}$  | 2816  |
| Crystal size (mm)                                  | 0.04 × 0.05 × 0.06  |
| Diffractometer                                     | Xcalibur S CCD  |
| $\theta$ range for data collection (°)             | 2.53–26.35  |
| Index ranges                                       | $-14 \leq h \leq 14, -14 \leq k \leq 14, -32 \leq l \leq 32$                              |
| Reflections collected                              | 26,347  |
| Independent reflections                            | 1048 ( $R_{\text{int}} = 0.1724$ )  |
| 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 <sup>3</sup> )    | 1.916 and -1.545  |

TABLE 3. Atom coordinates, equivalent isotropic displacement parameters ( $U_{\text{eq}}$ , Å<sup>2</sup>), site multiplicities ( $Q$ ) and site occupancy factors (s.o.f.) for chrysothallite.

| Atom               | $x/a$       | $y/b$       | $z/c$       | $U_{\text{eq}}$ | $Q$ | 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      |
| ' <i>Tl(2)</i> '** | ½           | ½           | ½           |                 | 2   | 1      |
| ' <i>Cl(6)</i> '** | 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 <sub>w</sub>     | 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  $2a$  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  $2a$  site '*Tl(2)*' and occupies one  $16m$  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)*'.

\*\*\*  $U_{\text{iso}}$ .

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(1)–Cl(2)       | 2.466(7) × 2  | ' <i>Tl(2)</i> '–' <i>Cl(6)</i> ' | 2.499 × 4*   |
| –Cl(1)            | 2.612(7) × 4  | –O <sub>w</sub>                   | 3.035 × 2*   |
| K(1)–Cl(4)        | 3.265(5) × 2  | O–H                               | 0.899(10)    |
| –Cl(3)            | 3.366(3) × 2  |                                   |              |
| –Cl(2)            | 3.382(5)      |                                   |              |
| –Cl(5)            | 3.441(6)      |                                   |              |
| –Cl(1)            | 3.457(4) × 2  |                                   |              |
| –' <i>Cl(6)</i> ' | 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 ↓ × 2 → × 4 |            | 0.22 ↓ × 2 | 0.45 ↓ × 4 |            | 0.99 |
| Cl(2)                             |            |                  | 0.10 → × 4       | 0.11       |            | 0.67 ↓ × 2 | 1.18       |      |
| Cl(3)                             | 0.48 ↓ × 2 |                  | 0.10 ↓ × 2 → × 2 |            | 0.21 ↓ × 4 |            |            | 0.89 |
| Cl(4)                             | 0.12 ↓ × 2 | 0.13 ↓ × 2 → × 2 | 0.13 ↓ × 2 → × 2 | 0.18 ↓ × 4 |            |            |            | 0.82 |
| Cl(5)                             |            | 0.42 ↓ × 2 → × 2 | 0.08             | 0.08 ↓ × 4 |            |            |            | 1.00 |
| 'Cl(6)'                           |            |                  | 0.12 → × 2       |            |            |            | 0.62 ↓ × 4 | 0.86 |
| O = OH                            | 0.41 ↓ × 2 | 0.45 ↓ × 2 → × 2 |                  |            |            |            |            | 1.31 |
| O <sub>W</sub> = H <sub>2</sub> O |            |                  |                  |            |            |            | 0.06 ↓ × 2 | 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'Keefe (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<sub>W</sub> shift and, thus, the 'Tl(2)' - O<sub>W</sub> distances become shorter.

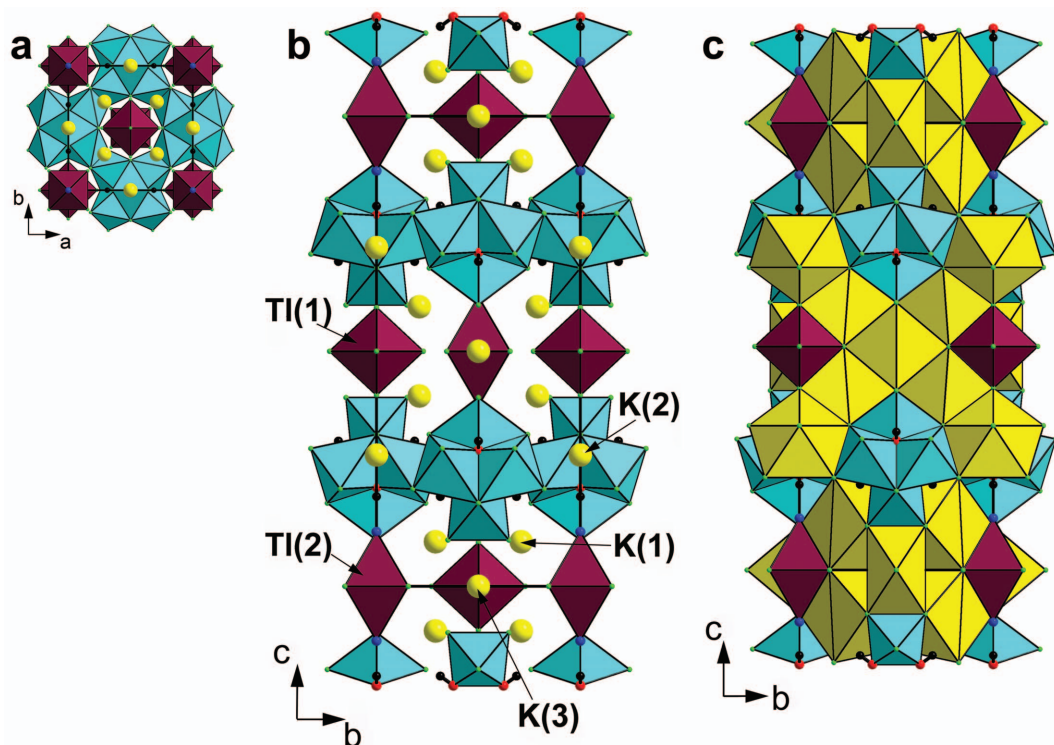


FIG. 5. The crystal structure of chrysothallite: (a) *ab* projection, (b) and (c) *bc* projection. Cu-centred polyhedra are turquoise-coloured, Cl atoms are green spheres, O atoms of OH groups are red spheres, H atoms of OH groups are black spheres and positions of O atoms belonging to H<sub>2</sub>O 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):  $\text{KTl}^{3+}\text{Cl}_4$  3.19–3.26,  $\text{K}_3\text{Tl}^{3+}\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  3.16–3.50,  $\text{K}_2\text{Tl}^{3+}\text{Cl}_5 \cdot 2\text{H}_2\text{O}$  3.15–3.67; this is in the same range as the  $\text{Tl}^+ - \text{Cl}^-$  distances.

Thus, there is no doubt that the thallium in chrysothallite is  $\text{Tl}^{3+}$ . 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  $\text{Fe}^{3+}$ ,  $\text{As}^{5+}$ ,  $\text{V}^{5+}$ ,  $\text{S}^{6+}$  and  $\text{Mo}^{6+}$ . Note that three new sulfate minerals with species-defining  $\text{Tl}^+$  were described recently from altered fumarolic deposits of the First scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption: markhininite  $\text{Tl}^+\text{Bi}(\text{SO}_4)_2$ , karpovite  $\text{Tl}_2^+\text{VO}(\text{SO}_4)_2(\text{H}_2\text{O})$  and evdokimovite  $\text{Tl}_4^+(\text{VO})_3(\text{SO}_4)_5(\text{H}_2\text{O})_5$  (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 180–200°C (typically 350–430°C, as our data show), only hydrogen-free minerals occur. Chrysothallite, which contains OH groups and H<sub>2</sub>O molecules, is associated with other hydrous minerals, such as belloite  $\text{CuCl}(\text{OH})$ , atacamite  $\text{Cu}_2\text{Cl}(\text{OH})_3$ , avdoninite  $\text{K}_2\text{Cu}_5\text{Cl}_8(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , eriochalcite  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , mitscherlichite  $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ , carnallite  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , natrochalcite  $\text{NaCu}_2(\text{SO}_4)_2[(\text{OH})(\text{H}_2\text{O})]$ , kröhnkite

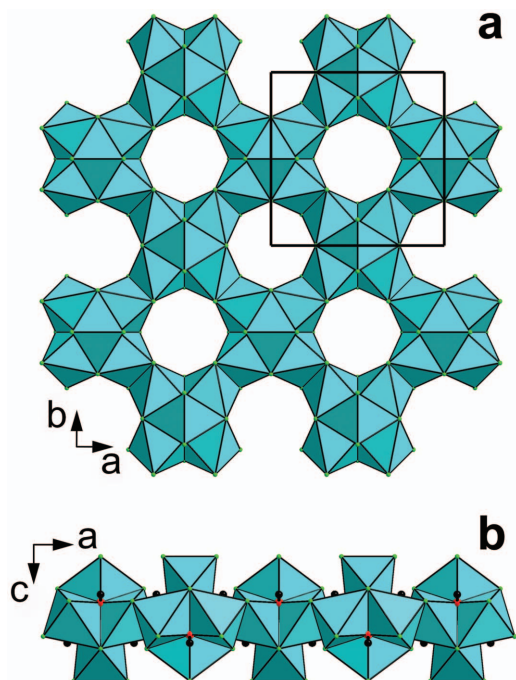


FIG. 6. The layer formed by Cu-centred polyhedra in chrysothallite: (a) *ab* projection, (b) *ac* projection. For legend see Fig. 5. The unit cell is outlined in (a).

$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  and antlerite  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ . 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%  $\text{H}_2\text{O}$ : 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  $>150^\circ\text{C}$ . In other words, the origin of chrysothallite can be characterized as a result of the combination of fumarolic and supergene processes. The presence of  $\text{Tl}^{3+}$  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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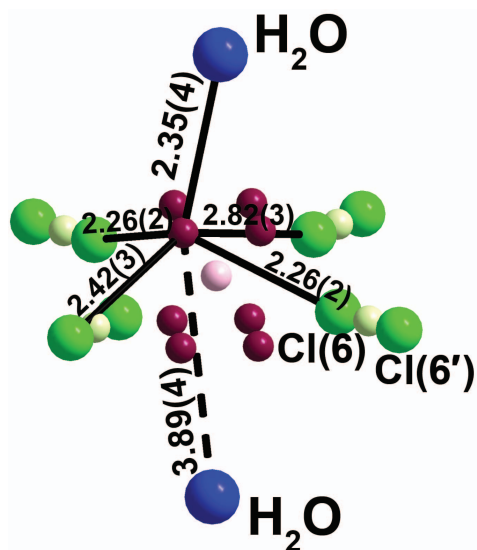


FIG. 7. Tl(2) cations (purple spheres) bound with O atoms of  $\text{H}_2\text{O}$  molecules, Cl(6) and Cl(6') anions. Pink and pale greenish spheres mark, respectively, the ‘Tl(2)’ and ‘Cl(6)’ positions in the idealized model (see Table 3). Bond lengths are given in Å.

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