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# Chloromenite, $Cu_9O_2(SeO_3)_4Cl_6$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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**Abstract:** Chloromenite, ideally $Cu_9O_2(SeO_3)_4Cl_6$, was found in a fumarole in the North Breakthrough of the Great Fissure Tolbachik eruption (1975-76, Kamchatka Peninsula, Russia). It occurs as transparent, tobacco-green crystals, tabular on $\{\bar{1}01\}$, elongated in [111] and $[1\bar{1}1]$, rarely in [010]; well-developed forms are {001}, {101}, $\{\bar{1}01\}$, {110}, {011}, $\{\bar{3}12\}$; forms $\{\bar{3}01\}$, {310} are poorly-developed. Associated minerals are melanothallite, an unknown scaly mineral, an unknown Se-containing mineral and weathering products. Chloromenite is plastic and has a perfect cleavage on (101), a strong vitreous luster and a yellowish-green streak. H = 27 kg/mm$^2$. The mineral is biaxial, optically negative; $\alpha$ = 1.87(1), $\beta$ = 1.92(1), $\gamma$ = 1.94(1), $2V_{meas}$ = 66(2)°, $2V_{calc}$ = 63°; orientation: Y = $\beta$, Z ~ $\gamma$. Pleochroism is clear in the green tones: $\alpha$ - green, $\beta$ - light brownish-green, $\gamma$ - black brownish-green.

Chloromenite is monoclinic, space group *I2/m*, *a* = 14.11(1), *b* = 6.274(2), *c* = 13.00(1) Å, $\beta$ = 113.0° (1), V = 1059 (2) Å$^3$, Z = 2, $D_x$ = 4.15(1) g/cm$^3$. The diagnostic lines of the X-ray powder diffraction pattern are (I-d-hkl): 63-11.3-$\bar{1}$01; 21-7.49-101; 17-6.51-200; 83-5.56-011; 100-3.45-103; 39-3.24-$\bar{2}$04; 33-2.71-$\bar{5}$03,312; 61-2.49-303,402. The crystal structure was solved by direct methods and refined to $R$ = 0.051 ($wR$ = 0.128). There are five copper positions in the chloromenite structure that correspond to five crystal chemically distinct coordination polyhedra: Cu(1), Cu(5) - the squares [2O + 2Cl] and [4O], Cu(2), Cu(4) - trigonal bipyramids [4O + Cl] and [5O], respectively, Cu(3) - a flattened tetrahedron [2O + 2Cl]. The structure is based on heteropolyhedral sheets parallel to (101) and composed of the $[Cu(2)O_4Cl]$, $[Cu(5)O_4]$ and $[Cu(1)O_2Cl_2]$ coordination polyhedra. The bipyramids $[Cu(2)O_4Cl]$ are linked through edges with two $[Cu(5)O_4]$ and one $[Cu(1)O_2Cl_2]$ squares. The sheets are linked together through the $[Cu(4)O_5]$ bipyramids and the $[Cu(3)O_2Cl_2]$ tetrahedra.

Microprobe analysis gave the following chemical composition (wt %): CuO 46.23 (45.33-46.83), ZnO 5.94 (5.76-6.03), $SeO_2$ 34.37 (33.48-35.56), Cl 16.57 (16.30-17.08), O = $Cl_2$ -3.74 (3.68-3.85), Σ 99.36 (98.90-99.69). The empirical formula, calculated from O + Cl = 20, $Cu_{7.71}Zn_{0.97}Se_{4.11}O_{13.80}Cl_{6.20}$, is close to the ideal one, $Cu_9O_2(SeO_3)_4Cl_6$, confirmed by the crystal structure analysis. The name chloromenite is chosen in accord with colour and chemical composition: χλωροζ – «green» (this also indicates that the mineral contains Cl) and μηναζ – «moon» (this indicates that the mineral contains Se).

**Key-words:** chloromenite, new mineral, oxide chloride selenite, Tolbachik Volcano, Kamchatka (Russia).

## Introduction

A new copper(II) oxide chloride selenite(IV), $Cu_9O_2(SeO_3)_4Cl_6$, has been discovered in a fumarole in the North Breakthrough of the Great Fissure Tolbachik eruption (GFTE) (1975-76, Kamchatka Peninsula, Russia). The mineral is named chloromenite according to its colour and chemical composition: χλωροζ – «green» (this also shows that the mineral contains chlorine) and

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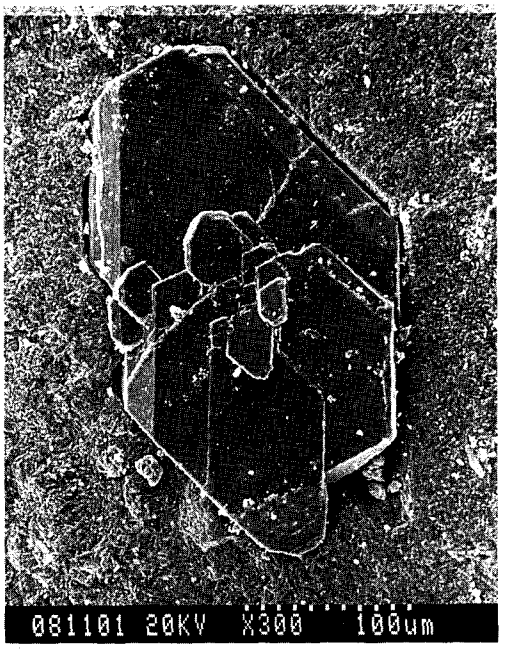


Fig. 1. SEM photographs of chloromenite crystals on the surface of melanothallite plates.

μηναζ – «moon» (selenium). Compare with chalcomenite $CuSeO_3 \cdot 2H_2O$, cobaltomenite, $CoSeO_3 \cdot 2H_2O$, *etc.* Type specimens are deposited in the Mineralogical Museum of the Department of Mineralogy, St.Petersburg State University, and the Mining Museum, Mining Institute, St. Petersburg. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (proposal no. 96-048). The mineral has no analogues in nature or as synthetic compounds.

## Locality and occurrence

The Great Fissure Tolbachik eruption (1975-76, Kamchatka Peninsula, Russia) is the greatest basaltic eruption in modern history. Its geology is described by Fedotov (1984). GFTE was active in 1975-76 and consists of two Breakthroughs (North and South) and seven cones. Chloromenite is found in the «new» fumarole, which occurred in 1977 on the west border of the 2nd North Breakthrough slag cone. The temperature of the gases in this fumarole in 1977 was about 700°C. The main mineral in the sample is melanothallite, $Cu_2OCl_2$ (Filatov & Vergasova, 1982), found as shapeless black plates substituted by a fine-grained green aggregate. Chloromenite occurs as elongate transparent plates up to 0.2 mm in length, growing on the surface of melanothallite crystals (Fig. 1). Other associated minerals are black-red needles of an unknown selenite, an unknown scaly green mineral and white weathering products on sophiite, $Zn_2(SeO_3)Cl_2$. Chloromenite is the third sublimate copper selenite found in the Tolbachik fumaroles. Two other copper oxide chloride selenites, georgbokiite, $Cu_5O_2(SeO_3)_2Cl_2$, and ilinskite, $NaCu_5O_2(SeO_3)_2Cl_3$, have recently been described by Vergasova *et al.* (1997, 1998) (approved by the Commission on New Minerals and Mineral Names, IMA, in 1996 (96-015 and 96-027, respectively)).

Table 1. Chemical composition of chloromenite (wt.%).

| Analysis | CuO | ZnO | $SeO_2$ | Cl | $-O=Cl_2$ | Σ |
|---|---|---|---|---|---|---|
| 1 | 45.33 | 5.76 | 35.56 | 16.47 | 3.72 | 99.40 |
| 2 | 46.83 | 5.94 | 34.20 | 16.42 | 3.70 | 99.69 |
| 3 | 46.17 | 6.03 | 33.48 | 17.08 | 3.85 | 98.90 |
| 4 | 46.58 | 6.03 | 34.24 | 16.30 | 3.68 | 99.47 |
| Mean | 46.23 | 5.94 | 34.37 | 16.57 | 3.74 | 99.36 |

## Chemistry

Chemical analyses of chloromenite were performed with a Camebax electron microprobe using an operating voltage of 20 kV and a beam current of 25 nA for all elements. The following standards were used for calibration: Cu (Cu), ZnSe (Zn, Se), halite (Cl). No elements other than those mentioned above have been detected. The results of the analyses are summarized in Table 1. The empirical formula of chloromenite, $Cu_{7.71}Zn_{0.97}Se_{4.11}O_{13.80}Cl_{6.20}$, calculated for O + Cl = 20, is close to the ideal one, $Cu_9O_2(SeO_3)_4Cl_6$, as confirmed by the crystal structure analysis (Krivovichev *et al.*, 1995, 1998).

## X-ray crystallography

Preliminary unit cell parameters of chloromenite were determined using a Weissenberg camera and were refined by X-ray powder diffraction method (DRON-2 diffractometer, Cu$K\alpha$ radiation, Ge standard). The experimental data, together with intensities calculated from the crystal structure, are given in Table 2. The intensities are significantly distorted due to the perfect

Table 2. X-ray powder diffraction pattern for chloromenite.

| $d_{obs}$, Å | $d_{calc}$*, Å | *hkl* | $I/I_{obs}$ | $I/I_{calc}$* |
|---|---|---|---|---|
| 11.29 | 11.28 | $\bar{1}\,0\,1$ | 63 | 65 |
| 7.49 | 7.47 | 1 0 1 | 21 | 12 |
| 6.51 | 6.50 | 2 0 0 | 17 | 35 |
| 5.56 | 5.56 | 0 1 1 | 83 | 81 |
| 4.311 | 4.315 | $\bar{1}\,0\,3$ | 19 | 23 |
| 3.643 | 3.644 | 3 0 1 | 25 | 26 |
| 3.450 | 3.454 | 1 0 3 | 100 | 72 |
| 3.239 | 3.241 | $\bar{2}\,0\,4$ | 39 | 25 |
| 3.133 | 3.136 | 0 2 0 | 25 | 100 |
| | 3.058 | $\bar{4}\,\bar{1}\,1$ | | 17 |
| 2.714 | 2.718 | $\bar{5}\,0\,3$ | 33 | 36 |
| | 2.704 | 3 1 2 | | 16 |
| 2.486 | 2.490 | 3 0 3 | 61 | 30 |
| | 2.479 | 4 0 2 | | 7 |
| 2.253 | 2.254 | $\bar{2}\,2\,4$ | 19 | 42 |
| 2.211 | 2.213 | $\bar{6}\,0\,4$ | 21 | 17 |
| 1.853 | 1.852 | 0 $\bar{3}$ 3 | 8 | 4 |
| 1.779 | 1.778 | $\bar{2}\,2\,6$ | 19 | 1 |

* $d_{calc}$ and $I/I_{calc}$ are based on the crystal structure determination

cleavage on (101). The diagnostic lines of the X-ray powder diffraction pattern are (I-d-hkl): 63-11.3-$\bar{1}$01; 21-7.49-101; 17-6.51-200; 83-5.56-011; 100-3.45-103; 39-3.24-$\bar{2}$04; 33-2.71-$\bar{5}$03,312; 61-2.49-303,402.

Chloromenite is monoclinic, space group *I2/m* (from crystal structure analysis; Krivovichev *et al.*, 1995, 1998). The unit cell parameters were refined from the positions of 15 reflections with $7^\circ \le 2\theta \le 52^\circ$ (Cu$K\alpha$ radiation). The refined unit cell parameters are $a$ = 14.11(1), $b$ = 6.274(2), $c$ = 13.00(1) Å, $\beta$ = 113.0° (1), V = 1059 (2) Å$^3$, Z = 2.

## Crystal structure

The crystal structure of chloromenite has been solved by direct methods in the space group *I2/m* and refined to $R$ = 0.051 ($wR$ = 0.128). The cell dimensions obtained by structure analysis [$a$ = 14.170(3), $b$ = 6.262(1), $c$ = 12.999(3) Å, $\beta$ = 113.05(1)°, V = 1061.3(4) Å$^3$] are in good agreement with those from powder diffraction data. A detailed description of the structure is given in Krivovichev *et al.* (1998). There are five copper positions in the chloromenite structure that correspond to five crystal chemically distinct coordination polyhedra: Cu(1) and Cu(5) - planar squares [2O + 2Cl] and [4O], Cu(2) and Cu(4) - trigonal bipyramids [4O + Cl] and [5O], respectively, Cu(3) - a flattened tetrahedron [2O + 2Cl]. In the [Cu(2)$O_4$Cl] polyhedron there are four oxygen atoms at 1.98-2.04 Å, whereas in the [Cu(4)$O_5$] bipyramid the equatorial oxygen atoms are at 2.03, 2.24, 2.24 Å. and the two apical ones at 1.90 and 1.95 Å. The refinement of the crystal structure does not show a preferable crystallographic posi-

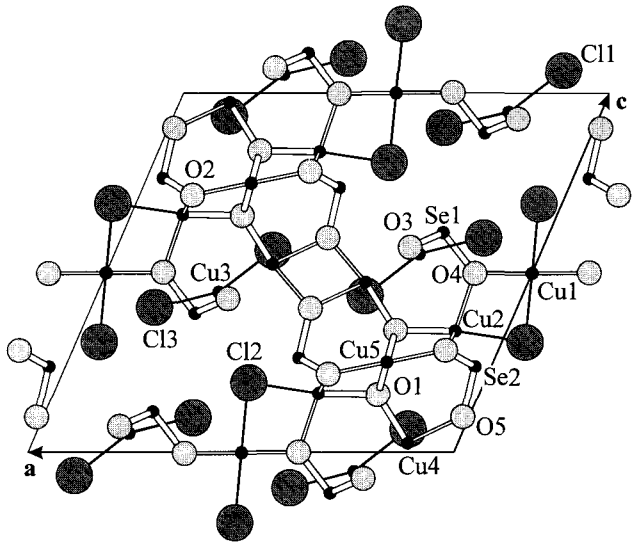


Fig. 2. Crystal structure of chloromenite projected onto the (010) plane.

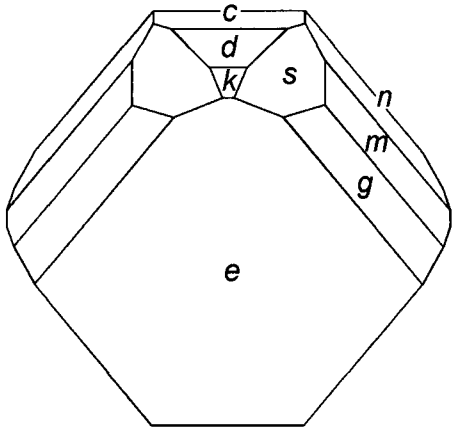


Fig. 3. Habit and crystal forms of chloromenite.

tion for zinc atoms. Therefore it has been proposed that zinc is statistically distributed among the copper positions. Both selenite groups have trigonal pyramidal coordinations with usual mean Se-O bond lengths of 1.70 Å.

Fig. 2 shows the chloromenite structure in the projection on the (010) plane. The structure is based on heteropolyhedral sheets parallel to (101) and composed of the $[Cu(2)O_4Cl]$, $[Cu(5)O_4]$ and $[Cu(1)O_2Cl_2]$ coordination polyhedra. The bipyramids $[Cu(2)O_4Cl]$ are linked through edges with two $[Cu(5)O_4]$ and one $[Cu(1)O_2Cl_2]$ squares. The sheets are linked together through the $[Cu(4)O_5]$ bipyramids and the $[Cu(3)O_2Cl_2]$ tetrahedra. The «additional» oxygen atom, O(1), is tetrahedrally coordinated by Cu(2), Cu(4) and two Cu(5) atoms with mean Cu-O bond length of 1.93 Å (1.90-1.98 Å). The mean bond length Cu-O for oxygen atoms of selenite groups, without regard for bonds longer than 2.20 Å, is 1.98 Å (1.90-2.04 Å). The copper atoms Cu(1) and Cu(3) are not bonded to O(1) at all. The crystal structure is discussed in more details in Krivovichev *et al.* (1998).

## Crystal morphology

The crystal morphology of chloromenite was studied by the measurement of 6 crystals with a 2-circle Goldschmidt reflection goniometer. Crystals of chloromenite grow in a plate-like habit flattened on $(\bar{1}01)$ and elongated along [111] and $[1\bar{1}1]$, rarely in [010]. Sometimes the crystals are isometric (Fig. 3). The well-developed forms are {001}, $\{\bar{1}01\}$, {101}, {110}, {011}, $\{\bar{3}12\}$; the forms $\{\bar{3}01\}$ and {310} are poorly developed. The angular coordinates for the faces of chloromenite crystals are given in Table 3. *a:b:c* relations calculated from morphology and from unit cell parameters are equal to 2.200 : 1 : 1.971 and 2.249 : 1 : 2.072, respectively. The $(\bar{1}01)$ plane has the highest reticular density. The unusual elongation of chloromenite (in [111] and $[1\bar{1}1]$) may be explained by the presence of *I*-translation in its lattice.

## Physical properties

The mineral is tobacco-green, with a strong vitreous luster and with a yellowish-green streak.

Chloromenite has a perfect cleavage parallel to the (101) plane, which is a plane of the strong copper heteropolyhedral sheets in the structure. The calculated density is 4.15(1) g/cm$^3$. The experimental density was not measured due to the small amount of material available.

The mineral is plastic. The hardness H = 27 kg/mm$^2$ was measured by micro-indentation (VHN load 5g, mean 62, range 60-63). Chloromenite is

Table 3. The angular coordinates (ϕ,ρ) for the crystal forms of chloromenite.

| Crystal form | *hkl* | Angular coordinates | | | |
|---|---|---|---|---|---|
| | | measured | | calculated | |
| | | ϕ | ρ | ϕ | ρ |
| *c** | {001} | 90°00′ | 23°58′ | 90°00′ | 23°05′ |
| *d** | {101} | 90°00′ | 55°52′ | 90°00′ | 55°23′ |
| *e** | $\{\bar{1}01\}$ | 90°00′ | 150°55′ | 90°00′ | 150°47′ |
| *m** | {110} | 24°34′ | 89°51′ | 25°49′ | 90°00′ |
| *n* | {011} | 12°18′ | 63°20′ | 12°05′ | 64°47′ |
| *k* | $\{\bar{3}01\}$ | 90°00′ | 110°52′ | 90°00′ | 106°08′ |
| *g** | {310} | 55°21′ | 89°52′ | 55°26′ | 90°00′ |
| *s** | $\{\bar{3}12\}$ | 46°23′ | 124°38′ | 45°39′ | 123°58′ |

* habit forms

soluble in cold diluted acids. The mineral does not fluoresce in short- or long-wave ultraviolet radiation.

## Optical properties

In transmitted light the mineral is transparent, biaxial and optically negative. The refractive indices were measured in immersion liquids and alloys: $\alpha$ = 1.87(1), $\beta$ = 1.92(1), $\gamma$ = 1.94(1), $2V_{meas}$ = 66(2)°, $2V_{calc}$ = 63°. It was possible to measure the 2V angle, because one of the optical axes is approximately normal to the cleavage plane. Optical orientation is Y = $\beta$, Z ~ $\gamma$. Chloromenite has a clear pleochroism in green tones: $\alpha$ - green, $\beta$ - light brownish-green, $\gamma$ - black brownish-green. The scheme of absorption is $\gamma > \alpha > \beta$.

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