

# Canutite, $\text{NaMn}_3[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2$ , a new protonated alluaudite-group mineral from the Torrecillas mine, Iquique Province, Chile

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## ABSTRACT

The new mineral canutite (IMA2013-070),  $\text{NaMn}_3[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2$ , was found at two different locations at the Torrecillas mine, Salar Grande, Iquique Province, Chile, where it occurs as a secondary alteration phase in association with anhydrite, halite, lavendulan, magnesiokoritnigite, pyrite, quartz and scorodite. Canutite is reddish brown in colour. It forms as prisms elongated on  $[20\bar{1}]$  and exhibiting the forms  $\{010\}$ ,  $\{100\}$ ,  $\{102\}$ ,  $\{201\}$  and  $\{10\bar{2}\}$ , or as tablets flattened on  $\{102\}$  and exhibiting the forms  $\{102\}$  and  $\{110\}$ . Crystals are transparent with a vitreous lustre. The mineral has a pale tan streak, Mohs hardness of  $2\frac{1}{2}$ , brittle tenacity, splintery fracture and two perfect cleavages, on  $\{010\}$  and  $\{101\}$ . The calculated density is  $4.112 \text{ g cm}^{-3}$ . Optically, canutite is biaxial (+) with  $\alpha = 1.712(3)$ ,  $\beta = 1.725(3)$  and  $\gamma = 1.756(3)$  (measured in white light). The measured  $2V$  is  $65.6(4)^\circ$ , the dispersion is  $r < v$  (slight), the optical orientation is  $Z = \mathbf{b}$ ;  $X \wedge \mathbf{a} = 18^\circ$  in obtuse  $\beta$  and pleochroism is imperceptible. The mineral is slowly soluble in cold, dilute HCl. The empirical formula (for tabular crystals from near the mine shaft), determined from electron-microprobe analyses, is  $(\text{Na}_{1.05}\text{Mn}_{2.64}\text{Mg}_{0.34}\text{Cu}_{0.14}\text{Co}_{0.03})_{\Sigma 4.20}\text{As}_3\text{O}_{12}\text{H}_{1.62}$ . Canutite is monoclinic,  $C2/c$ ,  $a = 12.3282(4)$ ,  $b = 12.6039(5)$ ,  $c = 6.8814(5) \text{ \AA}$ ,  $\beta = 113.480(8)^\circ$ ,  $V = 980.72(10) \text{ \AA}^3$  and  $Z = 4$ . The eight strongest X-ray powder diffraction lines are  $[d_{\text{obs}} \text{ \AA}(hkl)]$ :  $6.33(34)(020)$ ,  $4.12(26)(\bar{2}21)$ ,  $3.608(29)(310, \bar{1}31)$ ,  $3.296(57)(\bar{1}12)$ ,  $3.150(28)(002, 131)$ ,  $2.819(42)(400, 041, 330)$ ,  $2.740(100)(240, \bar{4}02, 112)$  and  $1.5364(31)$  (multiple). The structure, refined to  $R_1 = 2.33\%$  for  $1089 F_o > 4\sigma F$  reflections, shows canutite to be isostructural with protonated members of the alluaudite group.

**KEYWORDS:** canutite, new mineral, crystal structure, alluaudite group, Torrecillas mine, Chile.

## Introduction

OUR mineralogical investigation of the Torrecillas mine, a small, long-inactive As mine in the northern Atacama Desert of Chile, has shown it to host a remarkable secondary assemblage of rare

chlorides, arsenates and arsenites. Thus far, the deposit has yielded the new minerals leverettite,  $\text{CoCu}_3\text{Cl}_2(\text{OH})_6$  (Kampf *et al.*, 2013b; IMA2013-011), magnesiokoritnigite,  $\text{Mg}(\text{AsO}_3\text{OH})\cdot\text{H}_2\text{O}$  (Kampf *et al.*, 2013a; IMA2013-049) and torrecillasite,  $\text{Na}(\text{As,Sb})_4^3+\text{O}_6\text{Cl}$  (Kampf *et al.*, 2014; IMA2013-112). Herein, the new mineral canutite is described, a protonated arsenate member of the alluaudite group. Several more

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potentially new secondary arsenates and arsenites are currently under study.

Canutite is named in honour of Claudio Canut de Bon Urrutia (born in 1937), Chilean mining engineer and Senior Professor of Geology and Mineralogy at La Serena University for 30 years. He worked for 15 years as mining engineer for ENAMI (Chilean National Mining Corporation), assisting small-scale mine-development projects and conducting feasibility studies. A mine entrepreneur himself, he is President of La Serena Mining Association and a member of the SONAMI (Chilean National Society of Mining). Dr Canut has contributed extensively to the documentation of the history of Chilean mining, including authoring several books, publishing papers in scientific journals and making presentations at conferences. He is the biographer of Ignacio Domeyko, for whom the mineral domeykite is named. In 2011, he was awarded the Medal of Merit as a distinguished professional by the IIMCh (Chilean Institute of Mining Engineers). Dr Canut has agreed to the naming of the mineral in his honour.

The new mineral and the name have been approved by the International Mineralogical Association (IMA2013-070). Two cotype specimens are deposited in the Natural History Museum of Los Angeles, Los Angeles, California, USA, under catalogue numbers 64065 (from upper pit) and 64098 (from near shaft).

## Occurrence

The Torrecillas mine is located on Torrecillas Hill near Salar Grande, Iquique Province, Tarapacá Region, Chile (~20°58'13"S 70°8'17"W). Four different rock units are exposed on the hill. Rocks of the Coastal Range Batholith (mainly gabbros) extend from the seashore to the Pan-American Road along the base of the hill. At the foot of the hill is a small area of contact metamorphic rocks in which garnet crystals occur in metamorphosed shales. Higher on the hill, rocks are predominantly andesites and porphyritic lavas of the Jurassic La Negra Formation. The Torrecillas deposit, which the Torrecillas mine exploits, consists of two main veins rich in secondary As and Cu minerals that intersect metamorphosed marine shales and lavas. These veins are genetically related to the above-mentioned andesites and porphyritic lavas of the La Negra Formation. More information on the geology and mineralogy of the area is provided by Gutiérrez (1975).

The rare secondary chlorides, arsenates and arsenites have been found at three main sites on the hill: an upper pit measuring ~8 m long and 3 m deep, a lower pit ~100 m from the upper pit and measuring ~5 m long and 3 m deep and a mine shaft adjacent to the lower pit and lower on the hill. Canutite was first found by one of the authors (AAMD) in early 2012 in the upper pit (represented by cotype specimen 64065). Better crystals were collected by two of the authors (MD and AAMD) in July of 2013 from a small spot a few meters above the shaft (represented by cotype specimen 64098). Other potentially new alluaudite-group arsenates containing varying amounts of Na, Ca, Mg and Mn have also been identified in material collected from this deposit and these are currently under study.

Canutite from the upper pit is associated with anhydrite, halite, lavendulan and quartz. Canutite recovered from the small spot near the shaft is associated with anhydrite, halite, lavendulan, magnesiokoritinigite, pyrite and scorodite. The secondary assemblages at the Torrecillas deposit are interpreted as having formed from the oxidation of native As and other As-bearing primary phases, followed by later alteration by saline fluids derived from evaporating meteoric water under hyperarid conditions (*cf.* Cameron *et al.*, 2007).

## Physical and optical properties

Crystals of canutite are reddish brown (light reddish brown in PPL). Those from the upper pit occur as tapering prismatic to bladed crystals up

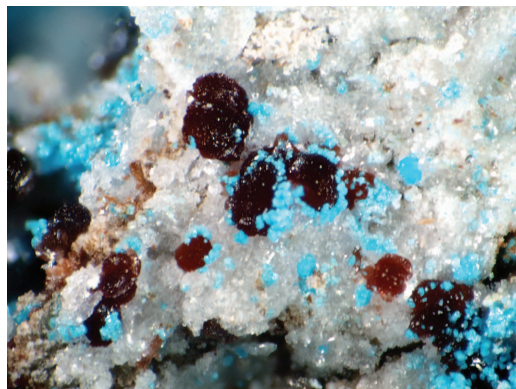


FIG. 1. Radial aggregates of canutite prisms with lavendulan (blue) on anhydrite, from the upper pit; field of view: 2 mm.

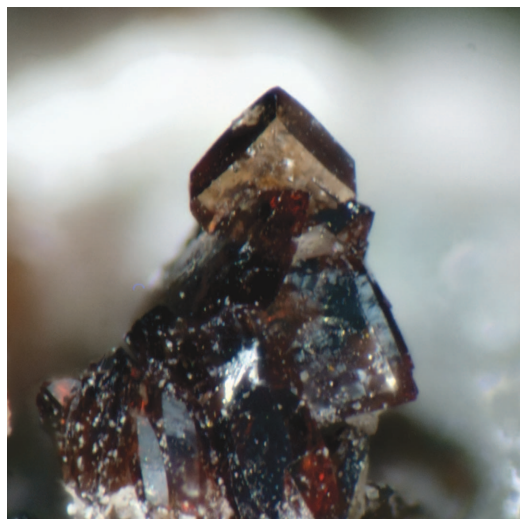


FIG. 2. Tabular canutite from near the shaft; field of view 0.75 mm.

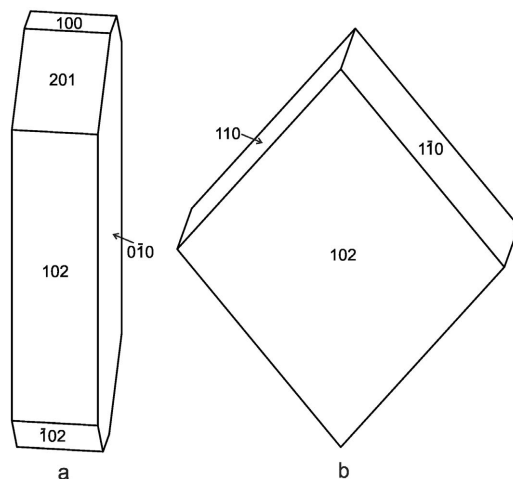


FIG. 3. Crystal drawings of canutite (clinographic projections in non-standard orientation,  $[20\bar{1}]$  vertical): (a) upper pit and (b) near shaft.

to  $\sim 0.2$  mm long grouped in tightly intergrown radial aggregates up to  $\sim 0.5$  mm in diameter (Fig. 1). The crystals from the small spot near the shaft occur as isolated and intergrown thin to thick diamond-shaped tablets up to  $\sim 0.2$  mm across (Fig. 2). The prismatic crystals from the upper pit are elongated on  $[20\bar{1}]$  and exhibit the forms  $\{010\}$ ,  $\{100\}$ ,  $\{102\}$ ,  $\{201\}$  and  $\{10\bar{2}\}$  (Fig. 3a). The tabular crystals from near the shaft are flattened on  $\{102\}$  and exhibit the forms  $\{102\}$  and  $\{110\}$  (Fig. 3b). Crystals are transparent with a vitreous lustre. The mineral has a pale tan streak. The Mohs hardness is  $2\frac{1}{2}$  based

on scratch tests. The tenacity is brittle, the fracture is splintery and there are two perfect cleavages, on  $\{010\}$  and  $\{101\}$ . The density could not be measured because there is insufficient material for direct measurement and crystals are nearly invisible in Clerici solution. The calculated density is  $4.112 \text{ g cm}^{-3}$  based on the empirical formula for crystals from near the shaft and  $4.119 \text{ g cm}^{-3}$  based on the ideal formula. The mineral is slowly soluble in cold, dilute HCl.

Optically, canutite is biaxial (+) with  $\alpha = 1.712(3)$ ,  $\beta = 1.725(3)$  and  $\gamma = 1.756(3)$  (measured in white light). The 2V measured

TABLE 1. Electron-microprobe analyses of canutite.

| Constituent                    | Upper pit; #64065 (5 analyses) |             |      | Near shaft; #64098 (25 analyses) |             |      |
|--------------------------------|--------------------------------|-------------|------|----------------------------------|-------------|------|
|                                | Wt.%                           | Range       | SD   | Wt.%                             | Range       | SD   |
| Na <sub>2</sub> O              | 3.82                           | 3.05–4.44   | 0.53 | 5.54                             | 4.86–6.30   | 0.32 |
| CaO                            | 0.52                           | 0.43–0.61   | 0.08 | 0.04                             | 0.00–0.15   | 0.03 |
| MgO                            | 2.91                           | 2.35–3.28   | 0.35 | 2.31                             | 1.34–4.31   | 0.99 |
| MnO                            | 27.88                          | 26.86–28.49 | 0.65 | 31.80                            | 27.32–34.40 | 1.94 |
| CoO                            | 2.52                           | 2.12–2.77   | 0.30 | 0.43                             | 0.28–0.61   | 0.08 |
| CuO                            | 1.40                           | 1.00–1.71   | 0.26 | 1.88                             | 1.24–2.62   | 0.41 |
| As <sub>2</sub> O <sub>5</sub> | 60.27                          | 58.99–61.40 | 1.06 | 58.45                            | 56.24–60.24 | 1.05 |
| H <sub>2</sub> O*              | 3.59                           |             |      | 2.48                             |             |      |
| Total                          | 102.91                         |             |      | 102.93                           |             |      |

\* Calculated on the basis of 3 As and 12 O a.p.f.u. and charge balance.

from extinction data using *EXCALIBUR* (Gunter *et al.*, 2004) is  $65.6(4)^\circ$  and the calculated  $2\theta$  is  $66.9^\circ$ . Dispersion is  $r < v$ , slight. The optical orientation is  $Z = \mathbf{b}$ ;  $X \wedge \mathbf{a} = 18^\circ$  in obtuse  $\beta$ . Pleochroism is imperceptible.

### Composition

Quantitative analyses were performed at the University of Utah using a Cameca SX-50 electron microprobe with four wavelength-disper-

sive spectrometers. Analytical conditions were 15 kV accelerating voltage, 20 nA beam current and beam diameters of 10 or 20  $\mu\text{m}$ . Counting times were 20 s on peak and 10 s on + and - background. Background positions were selected to account specifically for the proximity of the  $\text{AsL}\alpha_1$  and  $\text{MgK}\alpha_{1,2}$  peaks. No other elements were detected by EDS. Other probable elements were sought by EMPA, but none were above the detection limits. Raw X-ray intensities were corrected for matrix effects with a  $\phi(\rho z)$

TABLE 2. Powder X-ray data for canutite.

| $I_{\text{obs}}$ | $d_{\text{obs}}$ | $d_{\text{calc}}$ | $I_{\text{calc}}$ | $hkl$         | $I_{\text{obs}}$ | $d_{\text{obs}}$ | $d_{\text{calc}}$ | $I_{\text{calc}}$ | $hkl$         |
|------------------|------------------|-------------------|-------------------|---------------|------------------|------------------|-------------------|-------------------|---------------|
| 34               | 6.33             | 6.3020            | 42                | 0 2 0         |                  |                  | 1.8846            | 3                 | 6 0 0         |
| 15               | 5.67             | 5.6537            | 21                | 2 0 0         |                  |                  | 1.8636            | 11                | 1 5 2         |
| 6                | 4.45             | 4.4551            | 3                 | 1 1 1         | 12               | 1.8627           | 1.8540            | 4                 | $\bar{2}$ 4 3 |
| 6                | 4.20             | 4.2084            | 13                | 2 2 0         | 6                | 1.8430           | 1.8429            | 17                | 3 3 2         |
| 26               | 4.12             | 4.1087            | 18                | $\bar{2}$ 2 1 |                  |                  | 1.7782            | 4                 | 1 7 0         |
| 8                | 3.91             | 3.9382            | 12                | 1 3 0         |                  |                  | 1.7402            | 6                 | $\bar{1}$ 7 1 |
|                  |                  | 3.8266            | 5                 | $\bar{3}$ 1 1 | 15               | 1.7411           | 1.7326            | 3                 | 5 3 1         |
|                  |                  | 3.6111            | 29                | 3 1 0         | 16               | 1.7046           | 1.7060            | 21                | $\bar{2}$ 0 4 |
| 29               | 3.608            | 3.5711            | 8                 | $\bar{1}$ 3 1 |                  |                  | 1.6934            | 15                | $\bar{6}$ 4 2 |
|                  |                  | 3.3897            | 4                 | $\bar{2}$ 0 2 | 7                | 1.6878           | 1.6842            | 3                 | 1 7 1         |
| 57               | 3.296            | 3.2934            | 79                | $\bar{1}$ 1 2 |                  |                  | 1.6833            | 6                 | 5 5 0         |
|                  |                  | 3.1558            | 14                | 0 0 2         |                  |                  | 1.6722            | 3                 | $\bar{1}$ 5 3 |
| 28               | 3.150            | 3.1506            | 31                | 1 3 1         | 3                | 1.6680           | 1.6601            | 3                 | $\bar{4}$ 6 2 |
|                  |                  | 3.1024            | 6                 | 2 2 1         |                  |                  | 1.6219            | 3                 | $\bar{5}$ 1 4 |
| 13               | 3.015            | 3.0137            | 14                | $\bar{3}$ 1 2 | 3                | 1.6133           | 1.6022            | 5                 | 7 1 0         |
|                  |                  | 2.9852            | 4                 | $\bar{2}$ 2 2 |                  |                  | 1.5575            | 6                 | $\bar{3}$ 7 2 |
|                  |                  | 2.8269            | 21                | 4 0 0         |                  |                  | 1.5512            | 7                 | 4 4 2         |
|                  |                  | 2.8218            | 3                 | 0 2 2         |                  |                  | 1.5388            | 11                | $\bar{8}$ 0 2 |
| 42               | 2.819            | 2.8192            | 11                | 0 4 1         | 31               | 1.5364           | 1.5341            | 3                 | 2 4 3         |
|                  |                  | 2.8056            | 51                | 3 3 0         |                  |                  | 1.5286            | 4                 | 0 8 1         |
|                  |                  | 2.7654            | 3                 | $\bar{4}$ 2 1 |                  |                  | 1.5241            | 7                 | $\bar{5}$ 3 4 |
|                  |                  | 2.7524            | 56                | 2 4 0         |                  |                  | 1.5226            | 3                 | $\bar{7}$ 3 3 |
| 100              | 2.740            | 2.7094            | 27                | $\bar{4}$ 0 2 |                  |                  | 1.5120            | 12                | 3 7 1         |
|                  |                  | 2.7031            | 13                | 1 1 2         |                  |                  | 1.5092            | 7                 | 1 7 2         |
| 10               | 2.649            | 2.6486            | 40                | $\bar{1}$ 3 2 | 25               | 1.5098           | 1.5077            | 13                | 7 3 0         |
| 8                | 2.588            | 2.5792            | 16                | 4 2 0         |                  |                  | 1.5002            | 3                 | $\bar{2}$ 4 4 |
|                  |                  | 2.4891            | 3                 | $\bar{4}$ 2 2 |                  |                  | 1.4926            | 6                 | $\bar{4}$ 4 4 |
| 7                | 2.383            | 2.3812            | 9                 | 2 0 2         |                  |                  | 1.4519            | 4                 | 6 4 1         |
|                  |                  | 2.2259            | 13                | 5 1 0         |                  |                  | 1.4109            | 6                 | 0 4 4         |
|                  |                  | 2.2243            | 3                 | $\bar{3}$ 1 3 |                  |                  | 1.4086            | 5                 | 5 7 0         |
|                  |                  | 2.2017            | 4                 | $\bar{4}$ 4 1 | 19               | 1.4051           | 1.4021            | 12                | $\bar{1}$ 7 3 |
| 2                | 2.1027           | 2.0954            | 7                 | 3 5 0         |                  |                  | 1.3992            | 4                 | 1 3 4         |
| 13               | 2.0387           | 2.0373            | 16                | $\bar{5}$ 3 2 |                  |                  | 1.3922            | 6                 | 6 0 2         |
|                  |                  | 1.9913            | 3                 | 5 3 0         |                  |                  | 1.3838            | 5                 | 2 0 4         |
| 4                | 2.0008           | 1.9902            | 6                 | $\bar{3}$ 3 3 | 3                | 1.3858           | 1.3827            | 3                 | $\bar{8}$ 4 2 |
|                  |                  | 1.9586            | 3                 | $\bar{2}$ 6 1 |                  |                  | 1.3372            | 3                 | $\bar{8}$ 4 3 |
| 17               | 1.9629           | 1.9567            | 15                | $\bar{3}$ 5 2 | 6                | 1.3371           | 1.3334            | 9                 | $\bar{5}$ 7 3 |

Only calculated lines with intensities of 3 or greater are shown.

algorithm (Pouchou and Pichoir, 1991). The standards used were albite for Na, diopside for Ca and Mg, rhodonite for Mn, Co metal for Co, Cu metal for Cu and synthetic GaAs for As. Because insufficient material was available for a direct determination of H<sub>2</sub>O, the amount of water was calculated on the basis of 3 As and 12 O atoms per formula unit (a.p.f.u.), as determined by the crystal structure analysis (see below) and charge balance. Analytical data are given in Table 1 for samples from the upper pit and from near the shaft.

The empirical formula for material from the upper pit is (Na<sub>0.71</sub>Ca<sub>0.05</sub>Mn<sub>2.25</sub>Mg<sub>0.41</sub>Co<sub>0.19</sub>Cu<sub>0.10</sub>)<sub>Σ3.71</sub>As<sub>3</sub>O<sub>12</sub>H<sub>2.28</sub> and that for material from near the shaft is (Na<sub>1.05</sub>Mn<sub>2.64</sub>Mg<sub>0.34</sub>Co<sub>0.03</sub>Cu<sub>0.14</sub>)<sub>Σ4.20</sub>As<sub>3</sub>O<sub>12</sub>H<sub>1.62</sub>. Protonated arsenate members of the alluaudite group (see structure description below) have the general formula  $A_2M_1M_2[AsO_4][AsO_3(OH)]_2$ . In canutite, *A2* is

dominantly Na and both *M1* and *M2* are dominantly Mn, yielding the simplified structural formula NaMn<sub>3</sub>[AsO<sub>4</sub>][AsO<sub>3</sub>(OH)]<sub>2</sub>, which requires Na<sub>2</sub>O 5.11, MnO 35.08, As<sub>2</sub>O<sub>5</sub> 56.84, H<sub>2</sub>O 2.97, total 100 wt.%. The Gladstone-Dale compatibility index  $1 - (K_p/K_c)$  is 0.011 for the empirical formula for crystals from near the shaft and 0.019 for the ideal formula, in both cases in the range of superior compatibility (Mandarino, 2007).

### X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized MoK $\alpha$  radiation. For the powder-diffraction study, conducted on crystals from the upper pit, a Gandolfi-like motion on the  $\phi$  and  $\omega$

TABLE 3. Data collection and structure refinement details for canutite.

|   |  |
|---|--|
| Diffractometer                                | Rigaku R-Axis Rapid II   |
| X-ray radiation / power                       | MoK $\alpha$ ( $\lambda = 0.71075$ Å)/50 kV, 40 mA   |
| Temperature                                   | 298(2) K   |
| Structural formula                            | Na(Mn <sub>0.944</sub> Mg <sub>0.056</sub> ) <sub>Σ1.000</sub> (Mn <sub>1.570</sub> Mg <sub>0.266</sub> Co <sub>0.132</sub> -Cu <sub>0.032</sub> ) <sub>Σ2.000</sub> [AsO <sub>4</sub> ][AsO <sub>3</sub> (OH)] <sub>2</sub> |
| Space group                                   | C2/c   |
| Unit-cell dimensions                          | $a = 12.3282(4)$ Å<br>$b = 12.6039(5)$ Å<br>$c = 6.8814(5)$ Å<br>$\beta = 113.480(8)^\circ$<br>$V = 980.72(10)$ Å <sup>3</sup>   |
| <i>V</i>                                      | 980.72(10) Å <sup>3</sup>  |
| <i>Z</i>                                      | 4  |
| Density (for above formula)                   | 4.046 g cm <sup>-3</sup>   |
| Absorption coefficient                        | 13.666 mm <sup>-1</sup>  |
| <i>F</i> (000)                                | 1116.7   |
| Crystal size                                  | 170 x 110 x 70 $\mu$ m   |
| $\theta$ range                                | 3.23 to 27.48°   |
| Index ranges                                  | $-15 \leq h \leq 15$ , $-16 \leq k \leq 16$ , $-8 \leq l \leq 8$   |
| Refls collected / unique                      | 4789 / 1120; $R_{\text{int}} = 0.023$  |
| Reflections with $F_o > 4\sigma(F)$           | 1089   |
| Completeness to $\theta = 25.01^\circ$        | 99.1%  |
| Refinement method                             | Full-matrix least-squares on $F^2$   |
| Parameters refined                            | 91   |
| GoF   | 1.247  |
| Final <i>R</i> indices [ $F_o > 4\sigma(F)$ ] | $R_1 = 0.0233$ , $wR_2 = 0.0571$   |
| <i>R</i> indices (all data)                   | $R_1 = 0.0242$ , $wR_2 = 0.0576$   |
| Largest diff. peak / hole                     | +1.03 / -0.74 e/Å <sup>3</sup>   |

\*  $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$ . GoF =  $S = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$ .  $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ .  $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $a$  is 0.0313,  $b$  is 1.8035 and  $P$  is  $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$ .

TABLE 4. Atom coordinates and displacement parameters ( $\text{\AA}^2$ ) for canutite.

|     | $x/a$       | $y/b$       | $z/c$      | $U_{\text{eq}}$ | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{23}$     | $U^{13}$    | $U^{12}$    |
|-----|-------------|-------------|------------|-----------------|-------------|-------------|-------------|--------------|-------------|-------------|
| A2' | 0.0000      | 0.0068(3)   | 0.2500     | 0.0415(7)       | 0.0151(10)  | 0.094(2)    | 0.0133(10)  | 0.000        | 0.0035(9)   | 0.000       |
| M1* | 0.5000      | 0.21598(5)  | 0.2500     | 0.01082(15)     | 0.0099(3)   | 0.0115(3)   | 0.0118(3)   | 0.000        | 0.0051(3)   | 0.000       |
| M2* | 0.29298(4)  | 0.34086(4)  | 0.37881(8) | 0.01120(13)     | 0.0121(2)   | 0.0106(3)   | 0.0119(3)   | -0.00015(17) | 0.00585(19) | 0.00015(17) |
| As1 | 0.0000      | 0.31233(3)  | 0.2500     | 0.00882(12)     | 0.0100(2)   | 0.0089(2)   | 0.0063(2)   | 0.000        | 0.00189(16) | 0.000       |
| As2 | 0.21767(2)  | 0.11371(2)  | 0.11405(4) | 0.00834(11)     | 0.00997(17) | 0.00814(17) | 0.00638(17) | 0.00011(10)  | 0.00269(12) | 0.00008(10) |
| O1  | 0.35287(19) | 0.49819(17) | 0.4029(4)  | 0.0133(4)       | 0.0118(10)  | 0.0111(10)  | 0.0162(11)  | -0.0001(8)   | 0.0048(9)   | 0.0038(8)   |
| O2  | 0.36364(18) | 0.08994(18) | 0.1638(4)  | 0.0135(4)       | 0.0092(9)   | 0.0098(10)  | 0.0225(12)  | 0.0015(9)    | 0.0072(9)   | 0.00008(8)  |
| H   | 0.375(4)    | 0.025(2)    | 0.187(6)   | 0.016           |             |             |             |              |             |             |
| O3  | 0.11337(19) | 0.39439(17) | 0.2667(4)  | 0.0139(5)       | 0.0108(9)   | 0.0106(11)  | 0.0209(12)  | 0.0004(8)    | 0.0069(9)   | -0.0014(8)  |
| O4  | 0.34715(18) | 0.32454(17) | 0.1209(3)  | 0.0124(4)       | 0.0142(10)  | 0.0143(10)  | 0.0079(10)  | 0.0015(8)    | 0.0034(8)   | 0.0047(8)   |
| O5  | 0.21268(18) | 0.18657(17) | 0.3131(3)  | 0.0118(4)       | 0.0129(9)   | 0.0131(10)  | 0.0099(10)  | -0.0021(8)   | 0.0051(8)   | 0.0001(8)   |
| O6  | 0.03521(17) | 0.23829(18) | 0.4697(3)  | 0.0118(4)       | 0.0103(9)   | 0.0168(11)  | 0.0082(9)   | 0.0040(8)    | 0.0036(8)   | 0.0022(8)   |

\* The M1 site is occupied by 0.944 Mn and 0.056 Mg; the M2 site is occupied by 0.785 Mn, 0.133 Mg, 0.066 Co and 0.016 Cu.

TABLE 5. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for canutite.

|                       |          |                      |          |       |          |                       |          |        |          |
|-----------------------|----------|----------------------|----------|-------|----------|-----------------------|----------|--------|----------|
| A2'-O1 ( $\times 2$ ) | 2.355(2) | M1-O4 ( $\times 2$ ) | 2.209(2) | M2-O1 | 2.099(2) | As1-O6 ( $\times 2$ ) | 1.680(2) | As2-O5 | 1.671(2) |
| A2'-O1 ( $\times 2$ ) | 2.435(2) | M1-O2 ( $\times 2$ ) | 2.215(2) | M2-O4 | 2.141(2) | As1-O3 ( $\times 2$ ) | 1.705(2) | As2-O4 | 1.676(2) |
| A2'-O4 ( $\times 2$ ) | 2.878(3) | M1-O6 ( $\times 2$ ) | 2.216(2) | M2-O3 | 2.143(2) | <As-O>                | 1.693    | As2-O1 | 1.682(2) |
| A2'-O6 ( $\times 2$ ) | 3.235(4) | <M-O>                | 2.213    | M2-O5 | 2.147(2) |                       |          | As2-O2 | 1.719(2) |
| A2'-O5 ( $\times 2$ ) | 3.360(3) |                      |          | M2-O5 | 2.176(2) |                       |          | <As-O> | 1.687    |
| <A2'-O>               | 2.853    |                      |          | M2-O6 | 2.193(2) |                       |          |        |          |
|                       |          |                      |          | <M-O> | 2.150    |                       |          |        |          |
|                       |          |                      |          | D-H   | d(D-H)   |                       |          |        |          |
|                       |          |                      |          | O2-H  | 0.84(3)  |                       |          |        |          |
|                       |          |                      |          |       | d(D...A) |                       |          |        |          |
|                       |          |                      |          |       | 1.67(3)  |                       |          |        |          |
|                       |          |                      |          |       | d(DHA)   |                       |          |        |          |
|                       |          |                      |          |       | 175(4)   |                       |          |        |          |
|                       |          |                      |          |       | 2.505(3) |                       |          |        |          |
|                       |          |                      |          |       | A        |                       |          |        |          |
|                       |          |                      |          |       | O3       |                       |          |        |          |

axes was used to randomize the sample and observed  $d$  spacings and intensities were derived by profile fitting using *JADE 2010* software (Materials Data, Inc.). The powder data presented in Table 2 show good agreement with the pattern calculated from the structure determination. Unit-cell parameters refined from the powder data using *JADE 2010* with whole pattern fitting are  $a = 12.352(3)$ ,  $b = 12.623(3)$ ,  $c = 6.881(3)$  Å,  $\beta = 113.491(7)^\circ$  and  $V = 984.1(5)$  Å<sup>3</sup>.

Structure data were collected for crystals from both the upper pit and the area near the shaft. The *Rigaku CrystalClear* software package was used for processing structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005). *SHELXL-2013* (Sheldrick, 2008) was used for the refinement of the structure. Difference Fourier synthesis located the H atom position, which was refined with a soft restraint on the O2–H distance of 0.82(3) Å and with its  $U_{eq}$  set to  $1.2 \times$  that of O2. Both data sets yielded similar results; however, the larger size and better quality of the crystal from near the shaft provided a significantly larger data set. Consequently, only the results of that refinement are reported.

Although the empirical formula for the crystals from near the shaft indicates a cation excess of 0.2 a.p.f.u., there was no evidence of significant residual electron density in the channels of the structure to indicate where that excess might be accommodated. For that reason, the cation excess is attributed to analytical inaccuracy and, for purposes of assigning site occupancies, the

cations were normalized to Na + Mn + Mg + Co + Cu = 4 a.p.f.u. The  $A2'$  site was assigned full occupancy by Na. The  $M1$  and  $M2$  sites obviously accommodate Mn, Mg, Co and Cu. The occupancies of these sites were analysed using the program *OccQP* (Wright *et al.* 2001), which uses quadratic equations in a constrained least-squares formulation to optimize occupancy assignments based upon site scattering, chemical composition, charge balance, bond valence and cation–anion bond lengths. This analysis indicated the  $M1$  site to be occupied by 0.944 Mn and 0.056 Mg and the  $M2$  site to be occupied by 0.785 Mn, 0.133 Mg, 0.066 Co and 0.016 Cu. These site occupancies were used in the final refinement.

Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond-valence analysis in Table 6.

### Description of the structure

Canutite is a member of the alluaudite group and is isostructural with compounds with the protonated alluaudite-type structure, including the minerals o'danielite,  $\text{NaZn}_3[\text{AsO}_4][\text{AsO}_3(\text{OH})]_2$ , (Keller and Hess, 1988) and groatite,  $\text{NaCaMn}_2[\text{PO}_4][\text{PO}_3(\text{OH})]_2$ , (Cooper *et al.*, 2009). The general formula of these phases is  $A_2M_1M_2[T_1O_4][T_2O_3(\text{OH})]_2$  { $T = \text{P}$  or  $\text{As}$ }, where the  $M_1$  and  $M_2$  octahedra link by edge-sharing to form staggered chains,  $T_1$  and  $T_2$  tetrahedra cross-link the chains and  $A_2$  cations occupy large channel sites (Fig. 4). In canutite,  $T_1$  and  $T_2$  are As,  $M_1$  and  $M_2$  are dominantly Mn and  $A_2$  is dominantly Na.

TABLE 6. Bond-valence analysis for canutite. Values are expressed in valence units.

|            | O1   | O2                          | O3                          | O4                          | O5                          | O6                          | $\Sigma_c$ |
|------------|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|------------|
| $A2'$      | 0.22 $\times 2 \rightarrow$<br>0.18 $\times 2 \rightarrow$ |                             |                             | 0.05 $\times 2 \rightarrow$ | 0.01 $\times 2 \rightarrow$ | 0.02 $\times 2 \rightarrow$ | 0.96       |
| $M1$       |  | 0.31 $\times 2 \rightarrow$ |                             | 0.32 $\times 2 \rightarrow$ |                             | 0.31 $\times 2 \rightarrow$ | 1.88       |
| $M2$       | 0.41   |                             | 0.37                        | 0.37                        | 0.36<br>0.33                | 0.32                        | 2.16       |
| As1        |  |                             | 1.18 $\times 2 \rightarrow$ |                             |                             | 1.27 $\times 2 \rightarrow$ | 4.90       |
| As2        | 1.26   | 1.14                        |                             | 1.28                        | 1.30                        |                             | 4.98       |
| H          |  | 0.69                        | 0.31                        |                             |                             |                             | 1.00       |
| $\Sigma_a$ | 2.07   | 2.14                        | 1.86                        | 2.02                        | 2.00                        | 1.92                        |            |

Multiplicities indicated by  $\times 2 \rightarrow$ ; bond strengths based upon assigned site occupancies; bond strengths from Brown and Altermatt (1985); hydrogen-bond strengths based on O...O bond lengths from Brown and Altermatt (1985).

In the general alluaudite structure type, there are two channels running along the *c* axis. These channels can contain large monovalent and divalent cations, which may be placed at one or more of three sites in each channel. Channel 1 contains the *A1*, *A1'* and *A1''* sites and channel 2 contains the *A2*, *A2'* and *A2''* sites (Hatert *et al.*, 2000; Krivovichev *et al.*, 2013). In unprotonated alluaudites, both channels are occupied by large cations, while in protonated alluaudites, channel 1 is vacant, but contains the H atoms of the [T<sub>2</sub>O<sub>3</sub>(OH)] group. In canutite, Na occurs on the [0, *y*, ¼] (*y* ~ 0) position, corresponding to that of the *A2'* site, according to the site nomenclature established by Hatert *et al.* (2000) and revisited recently by Krivovichev *et al.* (2013). This site is the most frequently occupied in the channels of alluaudite-type compounds (Hatert *et al.*, 2003, 2005; Rondeux and Hatert, 2010; Hatert, 2006, 2008).

Arseniopleite is another arsenate belonging to the alluaudite group, in which both *M* sites are occupied dominantly by Mn. However, this arsenate is unprotonated and contains significant amounts of Ca in channel 1. Its simplified formula corresponds to (Ca,Na)(Na,Pb)Mn<sub>3</sub>(AsO<sub>4</sub>)<sub>3</sub> (Tait and Hawthorne, 2003); it can be considered as the unprotonated equivalent of canutite, with Ca instead of 2 H a.p.f.u.

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