## Weissite from Gambatesa mine, Val Graveglia, Liguria, Italy: occurrence, composition and determination of the crystal structure

L. BINDI<sup>1,2\*</sup>, C. CARBONE<sup>3</sup>, D. BELMONTE<sup>3</sup>, R. CABELLA<sup>3</sup> AND R. BRACCO<sup>4</sup>

<sup>1</sup> Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Florence, Italy

<sup>2</sup> CNR – Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Florence, Italy

<sup>3</sup> Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Università degli Studi di Genova, Corso Europa 26, I-16132 Genoa, Italy

<sup>4</sup> Via Montenotte 18, I-17100 Savona, Italy

[Received 23 April 2013; Accepted 5 May 2013; AE: A. Pring]

## ABSTRACT

Weissite,  $Cu_{2-x}Te(x \approx 0.21)$ , a very rare copper telluride, occurs in a sample from the Gambatesa mine, Val Graveglia, Liguria, Italy, where it occurs as purplish black anhedral grains up to 0.1 mm in length and shows a black streak. No cleavage is observed and the Vickers hardness (VHN<sub>100</sub>) is 142 kg/mm<sup>2</sup>. Weissite is dark bluish black, weakly pleochroic, and moderately anisotropic in bluish tints. Reflectance percentages in air for  $R_{min}$  and  $R_{max}$  are 37.0, 38.4 (471.1 nm), 33.2, 34.2 (548.3 nm), 31.2, 32.1 (586.6 nm), and 28.6, 31.0 (652.3 nm), respectively.

Weissite is trigonal and belongs to the space group P3m1 with the following unit-cell parameters: a = 8.3124(7) Å, c = 21.546(1) Å, V = 1289.3(2) Å<sup>3</sup>, and Z = 24. Electron microprobe analyses gave the chemical formula  $(Cu_{1.62}Ag_{0.04}Au_{0.04}Fe_{0.04}Sb_{0.04})_{\Sigma=1.78}(Te_{0.96}S_{0.02}Se_{0.02})$ . The crystal structure has been solved and refined to R = 1.95%. It consists of Cu and Te polyhedra forming complex crystal-chemical environments as is typical of many intermetallic compounds. The exceedingly short bond distances observed among the metals are discussed in relation to other copper tellurides and pure metals.

KEYWORDS: weissite, vulcanite, rickardite, tellurides, Val Graveglia, Italy.

## Introduction

WEISSITE,  $Cu_{2-x}Te$ , is a rare mineral first described by Crawford (1927) during a study of copper tellurides from the Good Hope and Mammoth Chimney mines at Vulcan, Gunnison County, Colorado, USA. The mineral was later studied by Thompson (1949), who carried out an X-ray powder diffraction study and pointed out the crystallographic and chemical differences with rickardite,  $Cu_{3-x}Te_2$ . By analogy with the synthetic compounds of the system Cu–Te (Patzak, 1956; Blachnik *et al.*, 1983), weissite

\* E-mail: luca.bindi@unifi.it DOI: 10.1180/minmag.2013.077.4.07 was considered to be hexagonal, with a = 12.54and c = 21.71 Å, and this description has persisted in the mineralogical literature (e.g. Anthony et al., 1990) as well as in several mineralogical databases. Some years later, Baranova et al. (1974) clarified the problem performing the structure determination of  $\beta^{III}$  by means of electron diffraction data, a synthetic compound with chemical formula Cu<sub>1 81</sub>Te and, therefore, considered the analogue of weissite. On this basis, Bayliss (1990) revised the unit cell and the crystal symmetry of weissite reporting the mineral as trigonal, with  $a \approx 8.3$  and  $c \approx 21.71$  Å. However, Pashinkin and Fedorov (2003) recently re-investigated all compounds in the system Cu-Te carefully and demonstrated that several

commensurate superstructures can occur for the  $Cu_{2-x}Te$  weissite-like compounds. Until now, no structural data have been reported for natural weissite. Furthermore, although correct (see below), the trigonal structural model obtained by Baranova *et al.* (1974) for synthetic  $Cu_{1.81}Te$  has a high *R* index (17.8%). To help resolve concerns relating to the physicochemical parameters of weissite, crystal structure data, together with physical and chemical data, are presented here.

# Occurrence and physical and optical properties

The sample containing the weissite crystal used in this study (Fig. 1) was found in 1998 in the dumps of the Gambatesa mine (Val Graveglia, northern Apennines, Liguria, Italy). The mineral occurs within late quartz veins cross-cutting red Jurassic cherts of the "Diaspri di Monte Alpe" Formation, which generally hosts Mn orebodies (Cabella *et al.*, 1998). The formation of secondary veins in the braunite-rich ore is genetically related to a tectonometamorphic overprint of the ophiolitic sequences during Late Cretaceous–Early Cenozoic at prehnite-pumpellyite facies conditions ( $T = 275\pm25^{\circ}$ C;  $P = 2.5\pm0.5$  kbar; Lucchetti *et al.*, 1990).

Weissite was identified because of the presence of olive-green patches of secondary minerals of mcalpineite (Carbone *et al.*, 2013). In the sample, weissite forms purplish black grains and veins in fractures of quartz up to a few mm thick, whereas its alteration products occur both as vein fillings and botryoidal aggregates on the faces of well developed quartz crystals. Minor chalcocite and



FIG. 1. Weissite from the Gambatesa mine as iridescent black grains in quartz. Picture 1.5 mm wide.

malachite are found rarely but not intimately associated with Cu-Te minerals.

The mineral exhibits a subhedral to anhedral grain morphology, and does not show any inclusions of, or intergrowths with, other minerals. The maximum grain size of weissite is  $\sim 100 \ \mu$ m. It has a black streak and it is opaque in transmitted light and exhibits a metallic lustre. No cleavage is observed and the fracture is uneven.

Micro-indentation measurements carried out with a VHN load of 100 g give a mean value of  $142 \text{ kg/mm}^2$  (range: 137-151) corresponding to a Mohs hardness of ~3.

In plane-polarized incident light, weissite is dark bluish black in colour, moderately bireflectant and very weakly pleochroic from light grey to a slightly greenish grey. Between crossed polars,

TABLE 1. Electron microprobe analyses (means, ranges and standard deviations) and atomic ratios (on the basis of one Te atom) for weissite.

	Wt.%	Ranges	σ	Atoms	Atomic ratios
Cu	41.50	39.55-41.99	0.16	Cu	1.62
Ag	1.80	1.55 - 2.01	0.03	Ag	0.04
Au	3.30	3.02-3.57	0.05	Au	0.04
Fe	0.94	0.77 - 1.11	0.03	Fe	0.04
Sb	2.04	1.85 - 2.29	0.04	Sb	0.04
Те	49.15	48.55-50.21	0.20	Те	0.96
S	0.27	0.12-0.35	0.02	S	0.02
Se	0.66	0.44 - 0.82	0.04	Se	0.02
Total	99.66	98.70-100.11		$\Sigma_{ m atoms}$	1.78

it is very weakly anisotropic with greyish to lightblue rotation tints. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by using an MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was ~3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages in air for  $R_{min}$ and  $R_{max}$  are 37.0, 38.4 (471.1 nm), 33.2, 34.2 (548.3 nm), 31.2, 32.1 (586.6 nm) and 28.6, 31.0 (652.3 nm), respectively.

### **Chemical composition**

A preliminary chemical analysis using energy dispersive spectroscopy, performed on the same crystal fragment used for the structural study, did not indicate elements (Z > 9) other than Cu, Te and very minor Ag, Au, Fe, Sb, Se and S. The chemical composition was then determined using a Jeol JXA-8600 electron microprobe. Concentrations of the major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with variable count times: 30 s were used for Cu and Te and

TABLE 2. Crystallographic data and refinement parameters for weissite.

Crystal data				
Ideal formula	$Cu_{2-x}Te \ (x = 0.21)$			
Crystal system	trigonal			
Space group	P3m1 (#156)			
Unit-cell parameters (Å)	8.3124(7) 21.546(1)			
Unit-cell volume $(Å^3)$	1289.3(2)			
Z	24			
Crystal size (mm)	$0.045\times0.050\times0.060$			
Data collection				
Diffractometer	Oxford Xcalibur 3			
Temperature (K)	298(3)			
Radiation, wavelength (Å)	ΜοΚα, 0.71073			
20 max for data collection (°)	69.87			
Crystal-detector dist. (mm)	50			
h, k, l ranges	-11 to 11, -13 to 13, -34 to 34			
Axis, frames, width (°), time per frame (s)	ω, 612, 1.00, 65			
Total reflections collected	22680			
Unique reflections $(R_{int})$	2163 (0.034)			
Unique reflections $I > 2\sigma(I)$	1224			
Data completeness to $\theta_{max}$ (%)	99.3			
Absorption correction method	ABSPACK (Oxford Diffraction, 2006)			
Structure refinement				
Refinement method	Full-matrix least-squares on $F^2$			
Data/restraints/parameters	2163/0/164			
$R_1 [I > 2\sigma(I)], wR_2 [I > 2\sigma(I)]$	0.0195, 0.0323			
$R_1$ all, $wR_2$ all	0.0227, 0.0425			
Goodness-of-fit on $F^2$	0.743			
Largest diff. peak and hole $(e^{-}/A^{3})$	0.69, -2.02			

$$\begin{split} R_{\rm int} &= (n/n - 1)^{1/2} [F_o^2 - F_o \, ({\rm mean})^2] / \Sigma F_o^2 \\ R_1 &= \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \, wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}; \\ * \, w &= 1 / [\sigma^2(F_o^2) + ({\rm aP})^2 + {\rm bP}], \, {\rm where} \, P = ({\rm max}(F_o^2, 0) + 2F_c^2) / 3; \\ {\rm GooF} &= \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2} \\ {\rm where} \, n \text{ is the number of reflections and } p \text{ is the number of refined parameters.} \end{split}$$

60 s for the minor elements Ag, Au, Fe, Sb, Se and S. For the wavelength dispersive spectroscopy analyses the following lines were used:  $CuK\alpha$ ,  $TeL\alpha$ ,  $AgL\alpha$ ,  $AuM\alpha$ ,  $FeK\alpha$ ,  $SbL\beta$ ,  $SeL\alpha$ and  $SK\alpha$ . The estimated analytical precision is:  $\pm 0.30$  for Cu and Te;  $\pm 0.02$  for Ag, Au, Sb and Se;  $\pm 0.01$  for Fe and S. The standards employed were: metallic copper (Cu), synthetic Sb<sub>2</sub>Te<sub>3</sub> (Sb, Te), metallic silver (Ag), metallic gold (Au), marcasite (Fe), synthetic PbSe (Se) and galena (S). The crystal fragment was found to be homogeneous within the limits of analytical uncertainty. The average chemical composition, together with ranges of wt.% of elements, is reported in Table 1. On the basis of  $\Sigma$ (Te+S+Se) = 1, the empirical formula is (Cu<sub>1.62</sub>Ag<sub>0.04</sub>Au<sub>0.04</sub> Fe<sub>0.04</sub>Sb<sub>0.04</sub>)<sub> $\Sigma$ =1.78</sub>(Te<sub>0.96</sub>S<sub>0.02</sub>Se<sub>0.02</sub>), ideally Cu<sub>2-x</sub>Te ( $x \approx 0.22$ ).

## Crystal-structure solution and refinement

A small crystal fragment (45  $\mu$ m × 50  $\mu$ m × 60  $\mu$ m) was selected for the single-crystal X-ray diffraction study. The intensity data collection (see

TABLE 3. Atoms, Wyckoff letter, site occupancy, fractional atom coordinates (Å), and isotropic atomic displacement parameters ( $Å^2$ ) for weissite.

Atom	Wyckoff	Site occupancy	x/a	y/b	z/c	$U_{\rm iso}$
Cu1	6 <i>e</i>	Cu <sub>0.17</sub>	0.4990(6)	-0.4990(6)	0.0010(4)	0.0370(9)
Cu2	1c	Cu <sub>1.00</sub>	2/3	1/3	0.04543(9)	0.0340(3)
Cu3	3 <i>d</i>	Cu <sub>1.00</sub>	0.8353(1)	-0.8353(1)	0.06099(7)	0.0406(2)
Cu4	1b	Cu <sub>1.00</sub>	1/3	2/3	0.06224(9)	0.0331(3)
Cu5	1a	Cu <sub>1.00</sub>	0	0	0.22505(8)	0.0329(3)
Cu6	3 <i>d</i>	Cu <sub>1.00</sub>	0.4961(1)	-0.4961(1)	0.22469(6)	0.0502(3)
Cu7	3 <i>d</i>	Cu <sub>0.50</sub>	0.1620(2)	-0.1620(2)	0.2540(1)	0.0511(5)
Cu8	3 <i>d</i>	Cu <sub>1.00</sub>	0.8250(1)	-0.8250(1)	0.27024(7)	0.0498(3)
Cu9	1b	Cu <sub>1.00</sub>	1/3	2/3	0.27094(6)	0.0323(3)
Cu10	1a	Cu <sub>1.00</sub>	0	0	0.32724(8)	0.0330(3)
Cu11	1c	Cu <sub>1.00</sub>	2/3		0.36849(8)	0.0322(3)
Cu12	3 <i>d</i>	Cu <sub>0.50</sub>	0.8310(2)	-0.8310(2)	0.4991(1)	0.0391(3)
Cu13	3 <i>d</i>	Cu <sub>1.00</sub>	0.16002(8)	-0.16002(8)	0.61992(6)	0.0399(2)
Cu14	1a	Cu <sub>1.00</sub>	0	0	0.67195(8)	0.0331(3)
Cu15	3 <i>d</i>	Cu <sub>1.00</sub>	0.4954(1)	-0.4954(1)	0.67486(7)	0.0506(3)
Cu16	1c	Cu <sub>1.00</sub>	2/3	1/3	0.69743(8)	0.0324(3)
Cu17	3 <i>d</i>	Cu <sub>1.00</sub>	0.8350(1)	-0.8350(1)	0.73079(7)	0.0506(3)
Cu18	1b	Cu <sub>1.00</sub>	1/3	2/3	0.73189(6)	0.0327(3)
Cu19	1a	Cu <sub>1.00</sub>	0	0	0.7779(1)	0.0329(3)
Cu20	3 <i>d</i>	Cu <sub>1.00</sub>	0.5049(1)	-0.5049(1)	0.77890(9)	0.0508(3)
Cu21	3 <i>d</i>	Cu <sub>1.00</sub>	0.1631(1)	-0.1631(1)	0.93206(8)	0.0501(3)
Cu22	3 <i>d</i>	Cu <sub>1.00</sub>	0.82801(8)	-0.82801(8)	0.93880(5)	0.0303(1)
Cu23	1b	Cu <sub>1.00</sub>	1/3	2/3	0.93969(9)	0.0334(3)
Cu24	1a	Cu <sub>1.00</sub>	0	0	0.99832(9)	0.0339(3)
Te1	1a	Te <sub>1.00</sub>	0	0	0.11395(4)	0.0331(2)
Te2	3 <i>d</i>	Te <sub>1.00</sub>	0.50500(5)	-0.50500(5)	0.11514(3)	0.0403(1)
Te3	3 <i>d</i>	Te <sub>1.00</sub>	0.83502(5)	-0.83502(5)	0.39005(3)	0.0405(1)
Te4	1b	Te <sub>1.00</sub>	1/3	2/3	0.39199(3)	0.0329(2)
Te5	1a	Te <sub>1.00</sub>	0	0	0.44201(4)	0.0330(2)
Te6	3 <i>d</i>	Te <sub>1.00</sub>	0.50499(5)	-0.50499(5)	0.44207(2)	0.0408(1)
Te7	3 <i>d</i>	$Te_{1.00}$	0.49705(6)	-0.49705(6)	0.55693(4)	0.0507(2)
Te8	1a	Te <sub>1.00</sub>	0	0	0.55787(4)	0.0331(2)
Te9	1b	Te <sub>1.00</sub>	1/3	2/3	0.60892(4)	0.0336(2)
Te10	3 <i>d</i>	Te <sub>1.00</sub>	0.82500(5)	-0.82500(5)	0.60891(2)	0.0409(1)
Te11	3 <i>d</i>	Te <sub>1.00</sub>	0.49495(5)	-0.49495(5)	0.88400(3)	0.0405(1)
Te12	1 <i>a</i>	Te <sub>1.00</sub>	0	0	0.88501(4)	0.0332(2)

## WEISSITE FROM LIGURIA

Table 2 for details) was carried out using an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (enhanced X-ray source, X-ray radiation MoK $\alpha$ ,  $\lambda = 0.71073$  Å) fitted with a Sapphire 2 CCD detector. A total of 612 frames of data were collected at room temperature as eight sets of omega runs with an exposure time of 65 s per frame and a frame width of 1.00°. This afforded an overall data collection of 22680 reflections (2163 unique). Data frames were processed using the *CrysAlis* software package (Oxford Diffraction, 2006) running on the Xcalibur 3 control PC. The program *ABSPACK* 

(Oxford Diffraction, 2006) was used for the absorption correction. The merging *R* for the data set decreased from 13.69% before the absorption correction to 3.40% after this correction. Because of the close similarity of the unit cell found with our instrument (i.e. a = 8.3124(7) Å, c = 21.546(1) Å, V = 1289.3(2) Å<sup>3</sup>) with that reported by Baranova *et al.* (1974) (a = 8.37 Å, c = 21.6 Å, V = 1310 Å<sup>3</sup>) for synthetic Cu<sub>1.81</sub>Te, we decided to solve the structure in the space group *P3m*1 as proposed by them. The positions of most of the Cu and Te atoms were determined from a three-dimensional Patterson synthesis (Sheldrick,

TABLE 4. Anisotropic displacement parameters of the atoms for the weissite crystal.

Atom	$U_{11}$	<i>U</i> <sub>22</sub>	U <sub>33</sub>	$U_{12}$	$U_{13}$	<i>U</i> <sub>23</sub>
Cu1	0.031(2)	0.031(2)	0.046(2)	0.013(2)	0.002(1)	-0.002(1)
Cu2	0.0339(4)	0.0339(4)	0.0342(6)	0.0170(2)	0	0
Cu3	0.0405(4)	0.0405(4)	0.0415(4)	0.0208(5)	0.0002(2)	-0.0002(2)
Cu4	0.0323(5)	0.0323(5)	0.0347(5)	0.0162(2)	0	0
Cu5	0.0337(5)	0.0337(5)	0.0313(6)	0.0168(2)	0	0
Cu6	0.0509(5)	0.0509(5)	0.0494(7)	0.0257(6)	-0.0006(3)	0.0006(3)
Cu7	0.0510(8)	0.0510(8)	0.049(1)	0.024(1)	-0.0006(5)	0.0006(5)
Cu8	0.0516(4)	0.0516(4)	0.0461(5)	0.0256(5)	0.0001(3)	-0.0001(3)
Cu9	0.0342(5)	0.0342(5)	0.0285(5)	0.0171(2)	0	0
Cu10	0.0328(5)	0.0328(5)	0.0335(6)	0.0164(3)	0	0
Cu11	0.0324(4)	0.0324(4)	0.0317(6)	0.0162(2)	0	0
Cu12	0.0380(6)	0.0380(6)	0.0419(6)	0.0195(8)	0.0002(4)	-0.0002(4)
Cu13	0.0402(3)	0.0402(3)	0.0380(3)	0.0192(4)	-0.0003(2)	0.0003(2)
Cu14	0.0318(5)	0.0318(5)	0.0359(7)	0.0159(2)	0	0
Cu15	0.0482(4)	0.0482(4)	0.0546(7)	0.0234(6)	-0.0003(2)	0.0003(2)
Cu16	0.0314(4)	0.0314(4)	0.0344(6)	0.0157(2)	0	0
Cu17	0.0522(5)	0.0522(5)	0.0479(8)	0.0266(6)	-0.0002(2)	0.0002(2)
Cu18	0.0332(5)	0.0332(5)	0.0316(6)	0.0166(2)	0	0
Cu19	0.0328(5)	0.0328(5)	0.0331(5)	0.0164(2)	0	0
Cu20	0.0508(5)	0.0508(5)	0.050(6)	0.0252(6)	-0.0003(2)	0.0003(2)
Cu21	0.0501(4)	0.0501(4)	0.0498(6)	0.0248(5)	-0.0002(2)	0.0002(2)
Cu22	0.0295(3)	0.0295(3)	0.0315(3)	0.0145(3)	-0.0003(2)	0.0003(2)
Cu23	0.0325(5)	0.0325(5)	0.0353(5)	0.0162(3)	0	0
Cu24	0.0344(5)	0.0344(5)	0.0331(5)	0.0172(2)	0	0
Te1	0.0331(3)	0.0331(3)	0.0331(3)	0.0165(1)	0	0
Te2	0.0404(2)	0.0404(2)	0.0400(2)	0.0203(2)	0.0003(1)	-0.0003(1)
Te3	0.0413(2)	0.0413(2)	0.0393(2)	0.0209(2)	0.00016(9)	-0.00016(9)
Te4	0.0339(2)	0.0339(2)	0.0308(3)	0.0170(1)	0	0
Te5	0.0336(3)	0.0336(3)	0.0319(3)	0.0168(1)	0	0
Te6	0.0411(2)	0.0411(2)	0.0399(2)	0.0204(2)	0.00035(9)	-0.00035(9)
Te7	0.0518(3)	0.0518(3)	0.0479(3)	0.0256(3)	-0.0004(1)	0.0004(1)
Te8	0.0337(2)	0.0337(2)	0.0319(3)	0.0169(1)	0	0
Te9	0.0344(3)	0.0344(3)	0.0319(3)	0.0172(1)	0	0
Te10	0.0414(2)	0.0414(2)	0.0397(2)	0.0205(2)	-0.0004(1)	0.0004(1)
Te11	0.0407(2)	0.0407(2)	0.0400(3)	0.0202(2)	-0.0004(1)	0.0004(1)
Te12	0.0337(2)	0.0337(2)	0.0324(4)	0.0168(1)	0	0



FIG. 2. The crystal structure of weissite projected down [100]. The horizontal direction is the c axis. Cu and Te are given as light blue and white spheres, respectively. The unit cell is outlined.

2008). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R factor of 16.21%. Threedimensional difference Fourier synthesis yielded the position of the remaining atoms. The fullmatrix least-squares program SHELXL-97 (Sheldrick, 2008) was used for the refinement of the structure. The occupancy of all the atoms were left free to vary and three Cu atoms (i.e. Cu1, Cu7 and Cu12) were found partially occupied, as in the model reported by Baranova et al. (1974). Then, their occupancy was fixed to the refined values to lower the number of refined parameters. The introduction of anisotropic temperature factors for all the atoms led to R = 1.95% for 1224 observed reflections [Fo >  $4\sigma(Fo)$ ] and R = 2.27% for all 2163 independent reflections. Neutral scattering curves for Cu and Te were taken from the International Tables for X-ray Crystallography (Ibers and Hamilton, 1974). Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 0.69 and 2.02  $e^{-}/Å^{3}$ , respectively. All the atoms were labelled with the same nomenclature given by Baranova et al. (1974).

Experimental details and *R* indices are given in Table 2. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Tables 3 and 4, respectively. Structure factors (Table 5) and bond distances (Table 6) have been deposited with the Principal Editor of *Mineralogical Magazine* at http://www.minersoc. org/pages/e\_journals/dep\_mat.html

### Description of the structure and discussion

The crystal structure of weissite (Figs. 2 and 3) is topologically identical to that reported by Baranova *et al.* (1974) for the synthetic  $\beta^{III}$ 

phase of the system Cu–Te. It can be considered as an intermetallic compound and, therefore, the classic polyhedral description is hardly applicable. There are 24 independent Cu and 12 Te atoms in the structure showing significantly different crystal-chemical environments (Table 7).

One of the most interesting structural peculiarities of the crystal structure of weissite, with respect to that of vulcanite (Pertlik, 2001) and rickardite (Schutte and de Boer, 1993), is the presence of exceedingly short bond distances between metals. The shortest Cu-Te distance in weissite of 2.308(2) Å (i.e. Cu19–Te12) is indeed much shorter than 2.604(1) Å and 2.63(1) Å observed in vulcanite (CuTe) and rickardite  $(Cu_{5-x}Te_2)$ , respectively. A similar behaviour is observed for the Cu-Cu and Te-Te contacts: the shortest Cu-Cu distance (i.e. Cu14-Cu19) of 2.282(3) Å is shorter than that observed in metallic copper (2.546 Å; Suh et al., 1988) and the shortest Te-Te distance (i.e. Te5-Te8) of 2.496(1) Å is shorter than that observed in native tellurium (Te-Te = 2.835 Å; Cherin and Unger, 1967).



FIG. 3. The crystal structure of weissite projected down [001]. The unit cell is outlined. Symbols and colours as in Figure 2.

#### WEISSITE FROM LIGURIA

Atom	Mean (Å)	Coordination
<cu1–te,cu></cu1–te,cu>	2.695	11-vertex polyhedron with 2Te and 9Cu
<cu2-te,cu></cu2-te,cu>	2.722	icosahedron with 3Te and 9Cu
<cu3-te,cu></cu3-te,cu>	2.711	bicapped square prism with 3Te and 7Cu
<cu4–te,cu></cu4–te,cu>	2.721	bicapped square prism with 3Te and 7Cu
<cu5-te,cu></cu5-te,cu>	2.493	8-vertex polyhedron with 1Te and 7Cu
<cu6–te,cu></cu6–te,cu>	2.504	trigonal prism with 1Te and 5Cu
<cu7–cu></cu7–cu>	2.533	pentagonal bipyramid with 7Cu
<cu8–te,cu></cu8–te,cu>	2.591	7-vertex polyhedron with 1Te and 6Cu
<cu9–te,cu></cu9–te,cu>	2.533	7-vertex polyhedron with 1Te and 6Cu
<cu10–te,cu></cu10–te,cu>	2.702	pseudo Frank-Kasper polyhedron with 4Te and 7Cu
<cu11–te,cu></cu11–te,cu>	2.622	tricapped trigonal prism with 6Te and 3Cu
<cu12–te></cu12–te>	2.613	8-vertex polyhedron wit 8Te
<cu13–te,cu></cu13–te,cu>	2.616	tricapped trigonal prism with 6Te and 3Cu
<cu14–te,cu></cu14–te,cu>	2.705	pseudo Frank-Kasper polyhedron with 4Te and 7Cu
<cu15-te,cu></cu15-te,cu>	2.707	pseudo Frank-Kasper polyhedron with 4Te and 7Cu
<cu16–te,cu></cu16–te,cu>	2.732	icosahedron with 3Te and 9Cu
<cu17–te,cu></cu17–te,cu>	2.634	8-vertex polyhedron with 1Te and 7Cu
<cu18–te,cu></cu18–te,cu>	2.653	7-vertex polyhedron with 1Te and 6Cu
<cu19–te,cu></cu19–te,cu>	2.603	trigonal bipyramid with 1Te and 4Cu
<cu20-te,cu></cu20-te,cu>	2.523	trigonal prism with 1Te and 5Cu
<cu21–te,cu></cu21–te,cu>	2.610	tricapped trigonal prism with 3Te and 6Cu
<cu22–te,cu></cu22–te,cu>	2.644	tricapped trigonal prism with 3Te and 6Cu
<cu23–te,cu></cu23–te,cu>	2.604	bicapped square prism with 3Te and 7Cu
<cu24–te,cu></cu24–te,cu>	2.711	11-vertex polyhedron with 2Te and 9Cu
<te1-cu></te1-cu>	2.722	bipyramid with 5Cu
<te2–cu></te2–cu>	2.740	trigonal prism with 6Cu
<te3–cu,te></te3–cu,te>	2.754	7-vertex polyhedron with 3Te and 4Cu
<te4–cu,te></te4–cu,te>	2.734	tetrahedron with 3Te and 1Cu
<te5–cu,te></te5–cu,te>	2.695	8-vertex polyhedron with 4Te and 4Cu
<te6–cu,te></te6–cu,te>	2.649	7-vertex polyhedron with 4Te and 3Cu
<te7–cu,te></te7–cu,te>	2.777	tricapped trigonal prism with 4Te and 5Cu
<te8–cu,te></te8–cu,te>	2.802	11-vertex-polyhedron with 4Te and 7Cu
<te9–cu,te></te9–cu,te>	2.683	bicapped square prism with 3Te and 7Cu
<te10-cu,te></te10-cu,te>	2.674	bicapped square prism with 3Te and 7Cu
<tell-cu></tell-cu>	2.655	pentagonal bipyramid with 7Cu
<te12–cu></te12–cu>	2.689	8-vertex polyhedron with 8Cu

TABLE 7. Mean bond distances (Å) and coordination polyhedra for weissite.

The reason for the formation of the superstructure characterizing the weissite structure (i.e. a superstructure of the basic hexagonal substructure with a = 4.25 and c = 7.29 Å, Villars and Calvert (1985)), as well as those of most of the phases in the system Cu–Te, is generally linked to the mobility of the copper ions in different valence states, Cu<sup>+</sup> or Cu<sup>2+</sup>, in a rigid Te framework. As documented by Pashinkin and Fedorov (2003), the arrangement of the Cu ions depends on the composition of the phase and thermal history, which may lead to the formation of a superstructure. Such features make the structural behaviour of weissite very similar to that of calaverite,  $AuTe_2$ , where the displacive modulation of the atoms is associated with a valence fluctuation of  $Au^+$  and  $Au^{3+}$  (Schutte and de Boer, 1988; Bindi *et al.*, 2009).

The origin of weissite is probably related to hydrothermal mobilization and concentration processes along fractures. Hydrothermal fluids have the ability to carry significant amounts of Te, as supported by the close Au-Te association in epithermal deposits (Pals and Spry, 2003) and experimental determinations as well (McPhail, 1995; Brugger *et al.*, 2012). In the Val Graveglia Mn-ores, the concentration of Te in the secondary veins seems to occur under reducing conditions, which are the same conditions responsible for the formation of the uncommon As-V parageneses previously described from ore deposits in Val Graveglia (Basso *et al.*, 1992, 1994, 2003, 2005, 2008; Bindi *et al.*, 2011).

#### Acknowledgements

The paper benefited from the official reviews of Allan Pring and Paul Spry.

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