Original paper

The role of hydrogen in tellurites: crystal structure refinements of juabite, poughite and rodalquilarite

Anthony R. KAMPF[1]*, Stuart J. MILLS[2]

[1] *Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A; email: akampf@nhm.org*
[2] *Geosciences, Museum Victoria, GPO Box 666, Melbourne 3001, Australia*
* *Corresponding author*

The crystal structures of the tellurite minerals juabite, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$, poughite, $Fe^{3+}_2(Te^{4+}O_3)_2(SO_4)(H_2O)_2 \cdot H_2O$ and rodalquilarite, $Fe^{3+}_2(Te^{4+}O_2OH)_3(Te^{4+}O_3)Cl$, have been refined to R_1 ($F_o > 4\sigma F$) = 2.36%, 2.38% and 1.84%, respectively. The determination of H atom positions in all three structures has allowed the elucidation of the hydrogen bonding schemes and detailed bond-valence analyses. These are the only tellurite mineral structures for which H atom positions have been determined. The structures of all contain one-sided Te^{4+} coordinations as $Te^{4+}O_3$ pyramids with additional anions at greater distances. The one-sided coordinations are attributable to the stereochemically active $6s^2$ lone-electron-pair of the Te^{4+}. The overall linkage schemes in these structures are quite different, yet all can be considered layer structures in which relatively weak long Te–O and/or Te–Cl bonds are involved in the linkages between layers. In juabite, a long apical Cu–O bond participates in the linkage between layers and, in poughite and rodalquilarite, hydrogen bonding also links the layers.

Keywords:crystal structure, juabite, poughite, rodalquilarite, $6s^2$ lone-electron-pair, hydrogen bonding
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1. Introduction

Tellurium oxysalt minerals are typically found in the oxidized portions of Au–Te ore deposits. In these minerals, Te occurs in 4+ and/or 6+ oxidation states. The tellurate group consists of Te^{6+} bonded to six O atoms in octahedral coordination. The tellurite group consists of Te^{4+} bonded to O atoms in typically one-sided coordinations. The most common tellurite configuration includes three short bonds to O atoms on one side, creating a pyramid with Te at its apex; however, there are also coordinations in which four and even five O atoms form relatively short bonds to Te^{4+}. These one-sided arrangements are attributable to a stereochemically active $6s^2$ lone-electron-pair of the Te^{4+}, which is positioned on the side opposite to the short Te–O bonds. The Te^{4+} coordinations usually include several additional O atoms, at significantly greater distances, on the same side as the lone-electron-pair.

Approximately 50 minerals are either known or presumed to contain tellurite groups and about one third of these also include H as OH and/or H_2O. Twenty-seven crystal structures of minerals with Te^{4+} have been determined and of these only nine have H atoms. Heretofore, H atom positions have not been determined for any mineral structures containing both tellurite groups and H_2O molecules, although they have been determined for the structure of rodalquilarite, $Fe^{3+}_2(Te^{4+}O_2OH)_2Cl$, in which OH is associated with the tellurite groups (Feger et al.

1999). Herein, we provide refinements of the structures of the hydrated tellurites juabite, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$, and poughite, $Fe^{3+}_2(Te^{4+}O_3)_2(SO_4)(H_2O)_2 \cdot H_2O$, in which we have been able to determine H atom positions. We also report a new refinement of the structure of rodalquilarite. The determination of the H atom positions can be essential in confirming the assignments of hydrogen bonds, which significantly contribute to the bond-valence balance. In turn, bond-valence analysis is useful in understanding the role of H atoms in Te^{4+} coordinations.

Juabite was first described by Roberts et al. (1997) from the Centennial Eureka mine, Juab County, Utah, and its structure (R_1 = 7.3%) was determined by Burns et al. (2000) using a crystal from the same specimen. Gaines (1968) provided the description of poughite from the Moctezuma mine, Sonora, Mexico, and Pertlik (1971) determined its structure (R = 8.2%) using a synthetic crystal. Rodalquilarite was first described by Sierra Lopez et al. (1968) from the Rodalquilar gold deposit, Almería Province, Spain, and Dusausoy and Protas (1969) reported its structure. The rodalquilarite structure (R_1 = 9.2%) was subsequently refined (R_1 = 3.9%) by Feger et al. (1999) using a synthetic crystal. The crystal of juabite used in the present study came from a specimen from the Gold Chain mine, Tintic district, Juab County, Utah, USA, provided by John Dagenais. The crystal of poughite came from a specimen from the Tambo mine, Coquimbo

Region, Chile provided by Maurizio Dini. The crystal of rodalquilarite came from a specimen in the collection of the Natural History Museum of Los Angeles County that originated from the Tambo mine, Coquimbo Region, Chile (catalogue #63508). The juabite and poughite specimens are now in the collection of the Natural History Museum of Los Angeles County, deposited under catalogue numbers 63509 and 63510, respectively.

2. Structure refinements

Single-crystal X-ray diffraction data for all three structure refinements were obtained at 298(2) K on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized MoK_α radiation (50 kV, 40 mA). The Rigaku CrystalClear software package was used for processing the structure data, including the application of shape-based and empirical absorption corrections. The starting atomic coordinates for the juabite refinement were taken from the structure determination by Burns et al. (2000), those for poughite from Pertlik (1971) and those for rodalquilarite (non-hydrogen) from Feger *et al.* (1999). SHELXL-97 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of the structures. Difference Fourier maps revealed the likely locations for all H atoms. The positions of the H atoms were constrained to H–O distances of 0.90(3) Å and H–H distances for water molecules to 1.45(3) Å. The isotropic displacement parameters for hydrogen atoms were held constant at 0.05 Å^2 in the structures of juabite and poughite, but were refined in the structure of rodalquilarite. All sites were assigned full occupancy except for the H6 site in rodalquilarite, which

Tab. 1 Data collection and structure refinement details for juabite, poughite and rodalquilarite

Species	juabite	poughite	rodalquilarite
Structural formula	$CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$	$Fe^{3+}_2(Te^{4+}O_3)_2(SO_4)(H_2O)_2 \cdot H_2O$	$Fe^{3+}_2(Te^{4+}O_2OH)_2(Te^{4+}O_3)Cl$
Space group	$P\bar{1}$	$P2_1nb$	$P\bar{1}$
Unit cell parameters			
a (Å)	8.9925(2)	9.6967(7)	5.11290(10)
b (Å)	10.1291(7)	14.2676(4)	6.6481(2)
c (Å)	8.9971(2)	7.8748(2)	9.0079(6)
α (°)	102.668(5)	–	73.347(5)
β (°)	92.490(6)	–	78.053(5)
γ (°)	70.434(5)	–	76.709(5)
Z	1	4	1
V (Å^3)	752.99(6)	1089.47(9)	282.20(2)
Density (g/cm^3)	4.50	3.74	5.02
Absorp. coefficient (mm^{-1})	15.4	8.2	13.0
$F(000)$	932	1128	376
Crystal size (μm)	280×50×20	70×70×8	140×80×30
range (°)	3.26 to 27.46	3.33 to 25.03	3.25 to 27.47
Index ranges			
	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-6 \leq h \leq 6$
	$-13 \leq k \leq 13$	$-16 \leq k \leq 16$	$-8 \leq k \leq 8$
	$-11 \leq l \leq 11$	$-8 \leq l \leq 9$	$-11 \leq l \leq 11$
Reflections coll./unique	23729 / 3435	9505 / 1917	8380 / 1291
R_{int}	0.0353	0.0532	0.0188
Reflections with $F_o > 4\sigma F$	3278	1785	1255
Completeness to θ_{max}	99.6%	99.6%	99.4%
Max. / min. transmission	0.75 / 0.10	0.94 / 0.60	0.70 / 0.26
Parameters refined	257	181	98
GoF	1.148	1.037	1.337
Weighting coefficients* a/b	0.0236 / 4.1785	0.0120 / 0.3335	0.0184 / 0.2120
Final R_1 index [$F_o > 4\sigma F$]	0.0236	0.0238	0.0146
Final wR_2 index [$F_o > 4\sigma F$]	0.0588	0.0444	0.0355
R_1 index (all data)	0.0250	0.0274	0.0156
wR_2 index (all data)	0.0595	0.0456	0.0360
Flack parameter		–0.01(3)	
Largest peak / hole (e/A^3)	+1.61 / –1.26	+0.58 / –0.56	+1.25 / –0.68

Notes: Refinement method: Full-matrix least-squares on F^2. $R_{int} = \Sigma|F_o^2 - F_o^2(mean)|/\Sigma[F_o^2]$. 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 P is $[2F_c^2 + Max(F_o^2, 0)]/3$

was assigned half occupancy because of its placement 0.405 Å from the center of symmetry at (0, ½, 0). Note that, although the difference Fourier syntheses showed multiple relatively high electron density residuals near all of the Te sites, they did not reliably predict the locations of the Te^{4+} lone pair electrons. Note also that, while Burns et al. (2000) noted a 20% excess in the occupancy of the Ca site in the juabite structure, our refinement showed no significant excess occupancy for this site.

The details of the data collections and structure refinements are provided in Tab. 1. The final atom coordinates and displacement parameters are listed in Tab. 2. Selected bond distances and angles are given in Tab. 3 and bond-valence analyses in Tab. 4.

3. Discussion of the crystal structures

3.1. General topology

The structures of juabite (Fig. 1), poughite (Fig. 2) and rodalquilarite (Fig. 3) all contain one-sided Te^{4+} coordinations as $Te^{4+}\Phi_3$ (Φ = O, OH) pyramids with additional anions at greater distances. The overall linkage schemes in these structures are quite different. Neglecting the Te^{4+} coordinations, the juabite structure consists of a framework of $Cu^{2+}\Phi_5$ (Φ = O, OH, H_2O) square pyramids, $Ca^{2+}O_6$ octahedra and AsO_4 tetrahedra; the poughite structure contains clusters of two edge-sharing $Fe^{3+}\Phi_6$ (Φ = O, H_2O) octahedra with a SO_4 tetrahedron; and the rodalquilarite structure contains edge-sharing chains of $Fe^{3+}O_6$ octahedra. The $Te^{4+}O_3$ pyramids link with octahe-

dra, square pyramids, and/or tetrahedra to form what in each case can be considered a layer structure.

In juabite, thick double-layers parallel to {010} link via the relatively weak long Te–O bonds of the Te^{4+} coordinations and the long apical bond of the $Cu4O_5$ square pyramid. The hydrogen bonding, described below, occurs within rather than between layers. In poughite, the layers are also parallel to {010}. They are linked to one another via long Te–O bonds, as well as via hydrogen bonding. One interlayer linkage is Te1–OW13–Te2, such that the OW13 can be considered an interlayer water molecule. In rodalquilarite, the layers are parallel to {001} and are linked to one another via weak Te–O and Te–Cl–Te bonds, as well as via an OH6–H6…OH6 hydrogen bond described below. Each of the three minerals has a perfect cleavage parallel to its layer direction.

Good general descriptions of the structures of juabite, poughite and rodalquilarite were provided by Burns et al. (2000), Pertlik (1971) and Feger et al. (1999), respectively. Herein, we will focus additional remarks on the Te^{4+} coordinations and the hydrogen bonding schemes, and we will examine how they relate to the overall bond-valence balance in each structure.

3.2. Te^{4+} coordinations

Each of the three structures contains two distinct Te^{4+} coordinations and all have one-sided bonding arrangements typical of Te^{4+} with stereochemically active lone-pair electrons (Fig. 4). All of the Te^{4+} coordinations have three short (*c*. 1.9 Å) bonds to O atoms on one side, forming a pyramid with the Te^{4+} at its apex. For Te^{4+}, as for other
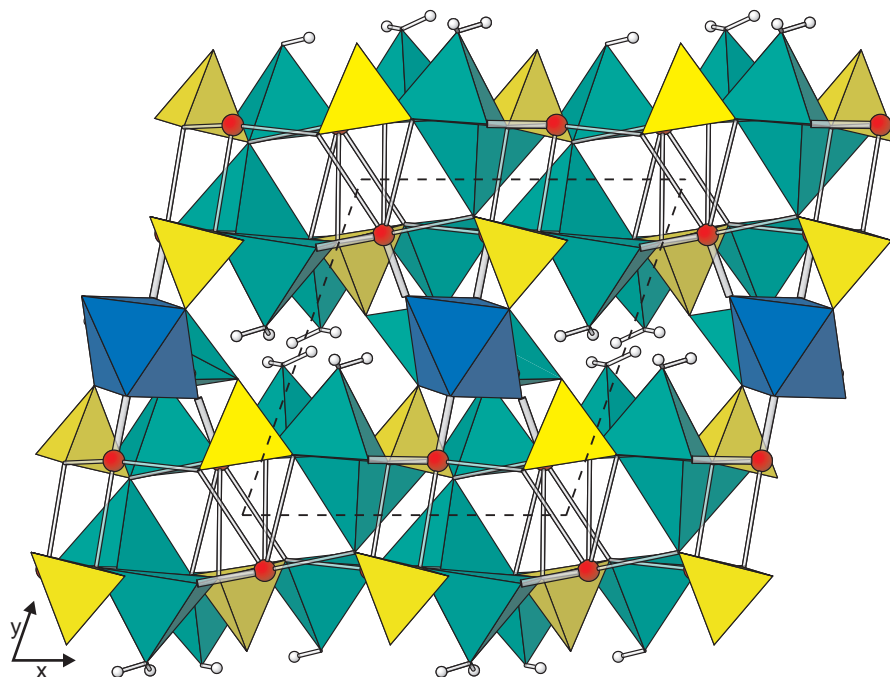
Fig. 1 Crystal structure of juabite along [001]. CaO_6 octahedra are shown in blue, $Cu^{2+}O_5$ square pyramids in green and AsO_4 tetrahedra in yellow. Te atoms appear as larger red spheres and H atoms as small white spheres. Short Te–O bonds of $Te^{4+}O_3$ pyramids are depicted as thick gray sticks.

Tab. 2 Fractional coordinates and atom displacement parameters (Å²) for juabite, poughite and rodalquilarite

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
juabite										
Ca	0.5000	0.5000	0.0000	0.0174(3)	0.0275(7)	0.0112(6)	0.0096(6)	0.0021(5)	−0.0006(5)	−0.0015(5)
Cu1	0.80847(6)	0.79847(6)	0.00221(6)	0.01053(11)	0.00822(2)	0.0178(3)	0.0067(2)	0.00412(19)	−0.00123(18)	−0.0050(2)
Cu2	0.29631(6)	0.84151(6)	0.51172(6)	0.00956(11)	0.0071(2)	0.0152(3)	0.0086(2)	0.0044(2)	−0.00175(18)	−0.0056(2)
Cu3	0.39218(6)	0.50715(6)	0.62469(6)	0.01284(12)	0.0124(3)	0.0114(3)	0.0135(3)	0.0044(2)	0.0011(2)	−0.0011(2)
Cu4	0.63366(6)	0.84877(6)	0.62919(6)	0.01128(11)	0.0077(2)	0.0217(3)	0.0072(2)	0.0049(2)	−0.00098(18)	−0.0073(2)
Cu5	−0.07412(6)	0.79869(6)	0.39124(6)	0.01257(12)	0.0085(2)	0.0242(3)	0.0073(2)	0.0039(2)	−0.00112(19)	−0.0082(2)
Te1	0.45602(3)	0.83827(3)	0.84848(3)	0.010331(7)	0.01015(14)	0.01328(14)	0.00919(13)	0.00333(10)	0.00061(10)	−0.00540(11)
Te2	0.12971(3)	0.83488(3)	0.17031(3)	0.015218(8)	0.01358(15)	0.02100(16)	0.01315(15)	0.00520(11)	0.00011(11)	−0.00748(12)
As1	0.06582(5)	0.77050(5)	0.72526(5)	0.008650(9)	0.00636(19)	0.0130(2)	0.00751(19)	0.00318(15)	−0.00038(15)	−0.00388(16)
As2	0.57354(5)	0.78999(5)	0.27256(5)	0.007310(9)	0.00623(19)	0.0102(2)	0.00642(19)	0.00284(15)	−0.00031(14)	−0.00332(15)
O1	0.9360(4)	0.7964(4)	0.1772(4)	0.0163(7)	0.0098(15)	0.0325(19)	0.0104(15)	0.0076(13)	−0.0028(12)	−0.0104(14)
O2	0.9955(4)	0.8138(4)	0.9048(3)	0.0173(7)	0.0123(15)	0.036(2)	0.0066(14)	0.0050(13)	−0.0002(12)	−0.0120(14)
O3	0.1835(4)	0.8663(4)	0.7093(3)	0.0134(6)	0.0109(14)	0.0192(16)	0.0120(15)	0.0026(12)	0.0002(12)	−0.0080(13)
O4	0.1208(4)	0.8388(4)	0.3848(4)	0.0154(7)	0.0104(15)	0.0314(19)	0.0097(14)	0.0088(13)	−0.0031(12)	−0.0114(14)
O5	0.6715(4)	0.8349(4)	0.8369(3)	0.0153(7)	0.0097(14)	0.0315(19)	0.0087(14)	0.0090(13)	−0.0018(11)	−0.0091(14)
O6	0.9079(4)	0.8216(4)	0.6126(3)	0.0133(6)	0.0077(14)	0.0264(18)	0.0064(14)	0.0045(12)	−0.0009(11)	−0.0059(13)
O7	0.4697(4)	0.8485(4)	0.6392(3)	0.0143(6)	0.0119(15)	0.0283(18)	0.0072(14)	0.0077(13)	−0.0028(11)	−0.0104(13)
OH8	0.3907(4)	0.5973(3)	0.4521(4)	0.0147(6)	0.0136(15)	0.0145(16)	0.0149(15)	0.0043(12)	−0.0017(12)	−0.0028(13)
H8	0.316(7)	0.578(8)	0.394(8)	0.050						
O9	0.3879(3)	0.8893(3)	0.3402(3)	0.0112(6)	0.0061(13)	0.0155(15)	0.0122(14)	0.0054(12)	0.0002(11)	−0.0024(12)
O10	0.6056(4)	0.8444(4)	0.1173(3)	0.0126(6)	0.0095(14)	0.0204(16)	0.0100(14)	0.0082(12)	−0.0007(11)	−0.0044(12)
O11	0.5985(4)	0.6138(3)	0.2261(4)	0.0145(6)	0.0188(16)	0.0111(15)	0.0151(15)	0.0047(12)	−0.0001(12)	−0.0060(13)
O12	0.2642(4)	0.6526(4)	0.1042(5)	0.0306(9)	0.0201(19)	0.028(2)	0.032(2)	−0.0051(17)	0.0017(16)	0.0003(16)
O13	0.1627(4)	0.5943(4)	0.6638(4)	0.0207(7)	0.0134(16)	0.0134(16)	0.034(2)	0.0052(14)	0.0010(14)	−0.0023(13)
O14	0.7041(4)	0.8183(4)	0.4081(3)	0.0146(6)	0.0083(14)	0.0287(18)	0.0082(14)	0.0034(13)	−0.0015(11)	−0.0088(13)
OW15	0.0394(6)	0.5528(5)	0.3541(6)	0.0405(11)	0.045(3)	0.028(2)	0.049(3)	0.005(2)	−0.010(2)	−0.017(2)
H15a	−0.035(7)	0.513(8)	0.335(8)	0.050						
H15b	0.088(8)	0.544(8)	0.439(6)	0.050						
OW16	0.8644(6)	0.5590(5)	0.9418(7)	0.0489(13)	0.048(3)	0.024(2)	0.067(4)	0.000(2)	−0.003(3)	−0.010(2)
H16a	0.786(7)	0.533(8)	0.965(7)	0.050						
H16b	0.885(9)	0.537(9)	0.841(4)	0.050						
O17	0.4873(4)	0.6464(4)	0.8254(4)	0.0182(7)	0.0255(18)	0.0148(16)	0.0173(16)	0.0054(13)	−0.0030(14)	−0.0095(14)

Tab. 2 continued

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
poughite										
Fe1	0.78997(11)	0.01378(7)	0.05942(13)	0.0119(2)	0.0084(5)	0.0186(5)	0.0087(6)	-0.0001(5)	-0.0003(5)	-0.0009(5)
Fe2	0.80679(12)	0.46555(7)	0.04731(14)	0.0112(2)	0.0095(5)	0.0145(5)	0.0096(5)	-0.0010(4)	0.0000(5)	-0.0004(5)
Te1	0.49972(4)	0.40022(3)	0.21999(6)	0.01141(13)	0.0082(3)	0.0160(2)	0.0100(3)	-0.00041(19)	-0.0003(3)	-0.0007(2)
Te2	0.07929(4)	0.09149(3)	0.21520(6)	0.01157(13)	0.0085(3)	0.0165(3)	0.0097(3)	0.00034(19)	-0.0003(3)	-0.0011(2)
S1	0.71579(19)	0.17290(12)	0.3354(2)	0.01132(4)	0.0138(9)	0.0132(9)	0.0124(9)	0.0006(7)	0.0034(8)	0.0013(7)
OW1	0.8956(6)	0.3372(3)	0.0717(7)	0.0230(12)	0.025(3)	0.021(3)	0.022(3)	0.002(2)	0.005(3)	0.010(3)
H1a	0.860(8)	0.288(4)	0.123(8)	0.050						
H1b	0.950(7)	0.322(5)	-0.014(7)	0.050						
OW2	0.3707(6)	0.1154(4)	0.0282(7)	0.0251(14)	0.035(4)	0.014(3)	0.026(3)	0.0022(2)	-0.012(3)	-0.002(3)
H2a	0.367(9)	0.169(3)	-0.025(9)	0.050						
H2b	0.423(8)	0.117(5)	0.120(7)	0.050						
O3	0.9178(5)	0.0193(3)	0.2609(6)	0.0121(11)	0.004(2)	0.021(3)	0.011(3)	0.001(2)	-0.001(2)	-0.004(2)
O4	0.6851(5)	0.4385(3)	0.2651(6)	0.0106(11)	0.008(3)	0.017(2)	0.007(3)	-0.002(2)	0.000(2)	-0.001(2)
O5	0.4276(6)	0.0137(4)	0.3607(7)	0.0162(13)	0.013(3)	0.023(3)	0.013(3)	0.002(2)	0.001(3)	0.009(2)
O6	0.1447(6)	0.0859(3)	0.4401(7)	0.0127(12)	0.008(2)	0.022(3)	0.008(3)	-0.003(2)	0.002(3)	0.004(2)
O7	0.4414(6)	0.4193(4)	0.4451(7)	0.0176(13)	0.017(3)	0.026(3)	0.010(3)	-0.001(2)	0.007(3)	0.003(2)
O8	0.1707(6)	0.4865(4)	0.3698(7)	0.0169(13)	0.011(3)	0.028(3)	0.012(3)	0.003(2)	-0.002(3)	0.001(2)
O9	0.7196(6)	0.0980(3)	0.4630(6)	0.0174(12)	0.019(3)	0.020(3)	0.014(3)	-0.001(2)	-0.001(3)	-0.001(2)
O10	0.6933(5)	0.1330(3)	0.1615(6)	0.0168(11)	0.018(3)	0.021(3)	0.011(3)	0.000(2)	0.001(2)	0.003(2)
O11	0.8479(4)	0.2239(3)	0.3382(6)	0.0188(12)	0.022(3)	0.015(3)	0.019(3)	0.001(2)	-0.001(2)	-0.006(2)
O12	0.6009(5)	0.2352(3)	0.3747(6)	0.0200(12)	0.016(3)	0.024(3)	0.021(3)	0.002(2)	0.008(2)	0.008(2)
OW13	0.2140(9)	0.2845(5)	0.2844(7)	0.0555(2)	0.097(6)	0.036(4)	0.031(4)	0.003(3)	-0.022(4)	-0.001(4)
H13a	0.231(8)	0.272(5)	0.391(5)	0.050						
H13b	0.166(9)	0.336(4)	0.271(9)	0.050						

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
rodalquilarite										
Fe	0.27611(8)	0.85489(6)	0.55577(5)	0.00733(10)	0.00710(19)	0.00701(18)	0.00800(19)	-0.00139(14)	-0.00182(15)	-0.00156(14)
Te1	0.12008(3)	0.34030(2)	0.68776(2)	0.00723(7)	0.00731(10)	0.00593(10)	0.00782(10)	-0.00117(7)	-0.00094(7)	-0.00083(6)
Te2	0.33841(3)	0.16581(3)	0.16967(2)	0.00894(7)	0.00901(11)	0.01131(11)	0.00728(11)	-0.00208(7)	-0.00083(7)	-0.00404(7)
O1	0.1934(4)	0.5929(3)	0.5382(2)	0.0096(4)	0.0151(10)	0.0058(8)	0.0088(9)	-0.0001(7)	-0.0034(8)	-0.0042(7)
O2	0.3628(4)	0.1361(3)	0.5839(2)	0.0103(4)	0.0079(9)	0.0090(9)	0.0146(10)	-0.0063(7)	0.0031(8)	-0.0027(7)
OH3	0.4048(4)	0.3169(3)	0.8053(2)	0.0127(4)	0.0146(10)	0.0097(9)	0.0157(11)	-0.0022(8)	-0.0071(9)	-0.0026(8)
H3	0.449(9)	0.441(5)	0.792(5)	0.031(12)						
O4	0.5437(4)	0.2849(3)	0.2623(2)	0.0130(4)	0.0177(11)	0.0108(9)	0.0128(10)	0.0007(8)	-0.0080(8)	-0.0068(8)
O5	0.1128(4)	0.0390(3)	0.3549(2)	0.0088(4)	0.0079(9)	0.0102(9)	0.0070(9)	-0.0003(7)	-0.0004(7)	-0.0018(7)
OH6*	0.0984(5)	0.4276(3)	0.1255(3)	0.0147(4)	0.0186(11)	0.0122(10)	0.0121(10)	-0.0018(8)	-0.0072(9)	0.0024(8)
H6**	0.06(3)	0.47(2)	0.028(7)	0.06(4)						
Cl	0.0000	0.0000	0.0000	0.0186(2)	0.0193(5)	0.0201(5)	0.0166(5)	0.0014(4)	-0.0044(4)	-0.0101(4)

* OH6 = $O_{0.5}(OH)_{0.5}$
** Assigned 0.5 occupancy.

Tab. 3 Selected bond distances (Å) and angles (°) for juabite, poughite and rodalquilarite

juabite

Cu1–O1	1.907(3)	Ca–O12 (×2)	2.259(4)
Cu1–O5	1.909(3)	Ca–O17 (×2)	2.361(3)
Cu1–O2	1.996(3)	Ca–O11 (×2)	2.398(3)
Cu1–O10	2.000(3)	<Ca–O>	2.339
Cu1–OW16	2.250(5)		
<Cu–O$_{eq}$>	1.953	Te1–O17	1.833(3)
		Te1–O7	1.920(3)
Cu2–O7	1.906(3)	Te1–O5	1.933(3)
Cu2–O4	1.912(3)	Te1–O3	2.661(3)
Cu2–O9	2.000(3)	Te1–O10	2.715(3)
Cu2–O3	2.011(3)	Te1–O10	3.021(3)
Cu2–OH8	2.276(3)	<Te–O$_{sh}$>	1.895
<Cu–O$_{eq}$>	1.957	<Te–O$_{lg}$>	2.799

Cu3–OH8	1.955(3)	Te2–O12	1.820(4)
Cu3–OH8	1.964(3)	Te2–O1	1.914(3)
Cu3–O13	1.967(3)	Te2–O4	1.926(3)
Cu3–O11	1.989(3)	Te2–O2	2.628(3)
Cu3–O17	2.353(3)	Te2–O9	2.866(3)
<Cu–O$_{eq}$>	1.969	Te2–O3	3.374(3)
		Te2–O6	3.510(3)
Cu4–O5	1.915(3)	Te2–O2	3.563(3)
Cu4–O7	1.931(3)	<Te–O$_{sh}$>	1.887
Cu4–O6	1.950(3)	<Te–O$_{lg}$>	3.188
Cu4–O14	1.952(3)		
Cu4–O9	2.466(3)	As1–O2	1.671(3)
<Cu–O$_{eq}$>	1.937	As1–O13	1.679(3)
		As1–O3	1.686(3)
Cu5–O1	1.926(3)	As1–O6	1.710(3)
Cu5–O4	1.933(3)	<As–O>	1.687
Cu5–O14	1.946(3)		
Cu5–O6	1.962(3)	As2–O10	1.679(3)
Cu5–OW15	2.307(5)	As2–O11	1.680(3)
<Cu–O$_{eq}$>	1.942	As2–O9	1.692(3)
		As2–O14	1.702(3)
		<As–O>	1.688

Hydrogen bonds (D = donor, A = acceptor)

D–H	d(D–H)	d(H…A)	<DHA	d(D…A)	A	<HDH
OH8–H8	0.88(3)	2.58(5)	153(7)	3.391(6)	OW15	
OW15–H15a	0.88(3)	1.83(4)	165(7)	2.688(6)	O13	
OW15–H15b	0.87(3)	2.11(4)	162(7)	2.949(6)	O13	116(5)
OW16–H16a	0.87(3)	2.04(6)	132(6)	2.707(7)	O12	
OW16–H16b	0.89(3)	1.84(4)	165(8)	2.709(8)	OW15	113(4)

poughite

Fe1–O8	1.889(6)	Te1–O5	1.874(5)
Fe1–O7	1.969(5)	Te1–O7	1.880(5)
Fe1–O3	2.015(5)	Te1–O4	1.912(5)
Fe1–O4	2.025(5)	Te1–O6	2.621(5)
Fe1–O10	2.102(5)	Te1–O12	2.827(5)
Fe1–OW2	2.118(5)	Te1–OW13	3.264(8)
<Fe–O>	2.020	Te1–O9	3.387(5)
		<Te–O$_{sh}$>	1.889
Fe2–O5	1.902(6)	<Te–O$_{lg}$>	3.025
Fe2–O6	1.929(5)		
Fe2–O3	2.006(5)	Te2–O8	1.864(5)
Fe2–OW1	2.033(5)	Te2–O6	1.883(5)
Fe2–O9	2.072(5)	Te2–O3	1.909(5)
Fe2–O4	2.117(5)	Te2–O7	2.517(6)
<Fe–O>	2.010	Te2–O11	3.089(4)
		Te2–OW13	3.097(7)
S–O12	1.458(5)	Te2–OW2	3.205(6)
S–O9	1.467(5)	<Te–O$_{sh}$>	1.885
S–O11	1.474(5)	<Te–O$_{lg}$>	2.977
S–O10	1.499(5)		
<S–O>	1.475		

Hydrogen bonds (D = donor, A = acceptor)

D–H	d(D–H)	d(H··A)	<DHA	d(D··A)	A	<HDH
OW1–H1a	0.87(3)	1.93(5)	144(7)	2.689(7)	O11	
OW1–H1b	0.88(3)	1.89(4)	157(8)	2.727(7)	O12	112(5)
OW2–H2a	0.87(3)	1.88(3)	173(7)	2.747(7)	O11	
OW2–H2b	0.89(3)	2.40(6)	130(6)	3.044(8)	O5	114(5)
		2.65(7)	132(7)	3.309(8)	O10	
OW13–H13a	0.88(3)	2.55(6)	132(6)	3.201(7)	O10	
		2.64(5)	139(6)	3.352(8)	OW1	113(5)
OW13–H13b	0.88(3)	2.28(6)	137(7)	2.989(8)	O8	

rodalquilarite

Fe–O4	1.938(2)	Te1–O1	1.887(2)	Te2–OH6	1.875(2)
Fe–O1	1.940(2)	Te1–OH3	1.925(2)	Te2–O4	1.884(2)
Fe–O2	2.010(2)	Te1–O2	1.932(2)	Te2–O5	1.916(2)
Fe–O5	2.029(2)	Te1–OH6	2.525(2)	Te2–O2	2.955(2)
Fe–O5	2.087(2)	Te1–O1	2.723(2)	Te2–Cl	3.0793(2)
Fe–O2	2.111(2)	Te1–Cl	3.1117(3)	Te2–OH3	3.115(2)
<Fe–O>	2.019	Te1–O5	3.170 (2)	Te2–OH3	3.137(2)
		Te1–OH3	3.617(2)	Te2–Cl	3.4791(2)
		<Te–O$_{sh}$>	1.915	<Te–O$_{sh}$>	1.892
		<Te–O$_{lg}$>	3.029	<Te–O$_{lg}$>	3.153

Hydrogen bonds (D = donor, A = acceptor)

D–H	d(D–H)	d(H…A)	<DHA	d(D…A)	A
OH3–H3	0.87(3)	1.76(3)	164(4)	2.604(3)	O4
OH6–H6	0.90(3)	1.64(5)	164(13)	2.510(4)	O6

Note: For the bond averages, the subscripts eq, sh and lg refer to equatorial, short and long bonds, respectively.

Tab. 4 Bond-valence analyses for juabite, poughite and rodalquilarite. Values are expressed in valence units

juabite

	Ca	Cu1	Cu2	Cu3	Cu4	Cu5	Te1	Te2	As1	As2	H8	H15a	H15b	H16a	H16b	Sum
O1		0.54				0.51		1.19								2.24
O2		0.42						0.17 + 0.01	1.30							1.90
O3			0.41				0.16	0.02	1.24							1.83
O4			0.53			0.50		1.15								2.18
O5		0.54			0.53		1.13									2.20
O6					0.48	0.47		0.01	1.17							2.13
O7			0.54			0.51	1.17									2.22
OH8			0.20	0.47 + 0.46							0.96					2.09
O9			0.42		0.12			0.09		1.22						1.85
O10		0.42					0.14 + 0.06			1.27						1.89
O11	0.31 ×2↓			0.43						1.27						2.01
O12	0.45 ×2↓							1.53						0.11		2.09
O13				0.46					1.27			0.18	0.10			2.01
O14					0.48	0.49				1.20						2.17
OW15							0.18				0.04	0.82	0.90		0.17	2.11
OW16		0.21												0.89	0.83	1.93
O17	0.34 ×2↓			0.16			1.48									1.98
Sum	2.20	2.13	2.10	1.99	2.11	2.15	4.14	4.17	4.98	4.95	1.00	1.00	1.00	1.00	1.00	

poughite

	Fe1	Fe2	Te1	Te2	S	H1a	H1b	H2a	H2b	H13a	H13b	Sum
OW1		0.48				0.86	0.84			0.04		2.22
OW2	0.38			0.04				0.84	0.90			2.16
O3	0.50	0.51		1.20								2.21
O4	0.49	0.38	1.19									2.06
O5		0.68	1.32						0.06			2.06
O6		0.63	0.18	1.29								2.10
O7	0.57		1.30	0.23								2.10
O8	0.70		1.36								0.08	2.14
O9		0.43	0.02		1.53							1.98
O10	0.40				1.40				0.04	0.05		1.89
O11			0.05	1.50		0.14		0.16				1.85
O12			0.10	1.57			0.16					1.83
OW13			0.03	0.05						0.91	0.92	1.91
Sum	3.03	3.11	4.14	4.22	6.00	1.00	1.00	1.00	1.00	1.00	1.00	

rodalquilarite

	Fe	Te1	Te2	H3	H6	Sum
O1	0.61	1.28 + 0.13				2.02
O2	0.51 + 0.39	1.13	0.07			2.10
OH3		1.15 + 0.01	0.05 + 0.04	0.80		2.05
O4	0.62		1.29	0.20		2.11
O5	0.48 + 0.41	0.04	1.18			2.11
OH6		0.23	1.32		0.75 ×½→ + 0.25 ×½→	2.05
Cl		0.14 ×2→	0.15 ×2→ + 0.05 ×2→			0.66
Sum	3.02	4.11	4.15	1.00	1.00	

Notes: Multiplicity is indicated by ×→↓; Ca^{2+}–O, Cu^{2+}–O, Fe^{3+}–O, As^{5+}–O, S^{6+}–O and Te^{4+}–O bond strengths from Brown and Altermatt (1985); hydrogen-bond strengths based on H–O bond lengths, also from the same work.
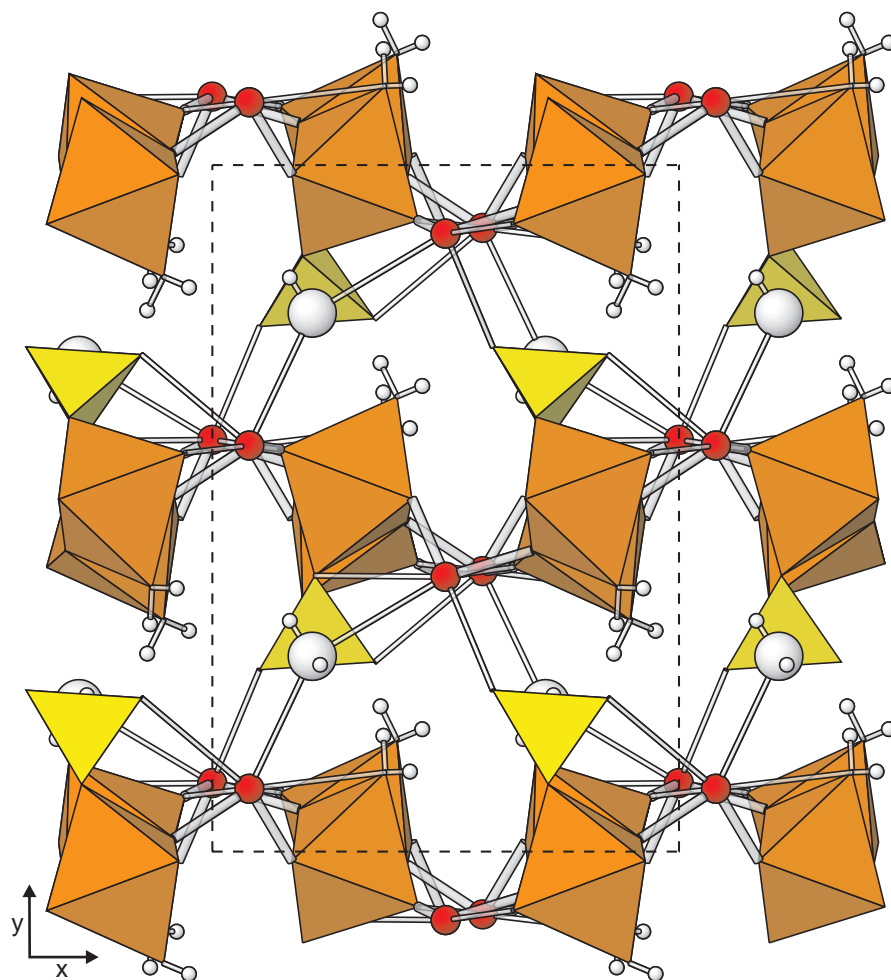
cations with stereochemically active lone-pair electrons (e.g., Pb^{2+}), it is often difficult to decide how far to extend the coordination sphere. Coordination geometry and bond-valence summations (BVS) provide useful guidance in this regard.

In their study of the juabite structure, Burns et al. (2000) only included O atoms at distances of 3.04 Å or less from the Te^{4+}, yielding coordinations of 3 + 3 and 3 + 2 (short + long) for Te1 and Te2, respectively. We prefer to extend the coordination sphere when the geometry warrants. Herein, we report the same 3 + 3 coordination for Te1, but extend the coordination of Te2 to include O atoms at distances of 3.374, 3.510 and 3.563 Å, all placed on the same side of Te2 as the presumed lone pair electrons, yielding 3 + 5 coordination.

Pertlik (1971) reported 3 + 1 coordinations with maximum Te–O distances of 2.70 Å; however, this was before methods for detailed bond-valence analysis were available. The BVS for Te1 and Te2 based upon their coordinations and bond distances are 3.73 and 4.14 *vu* (valence units), respectively, although it should be noted that the same coordinations with the bond distances from our re-

finement of the structure yield 3.99 and 4.08 *vu*. Indeed, the weakly bonded distant O atoms in Te^{4+} coordinations can generally be ignored without much effect on the BVS of the Te^{4+}; however, again for poughite, we think it more realistic to include those O atoms at somewhat greater distances. We herein report 3 + 4 coordinations for Te1 and Te2, with Te^{4+}–O distances up to 3.387 Å and BVS of 4.14 and 4.22 *vu* for Te1 and Te2, respectively.

The Te^{4+} coordinations in rodalquilarite include both O and Cl atoms. In both coordinations, the three short bonds are to O atoms. Feger et al. (1999) mistakenly assigned two equivalent Cl atoms to each Te^{4+} of the coordinations; however, in fact, there is only one in each case. Neglecting the duplicate atoms, Feger et al. (1999) reported 3 + 3 and 3 + 2 coordinations including one distant Cl atom in each coordination, out to a maximum Te–O distance of 2.963 Å and a maximum Te–Cl distance of 3.113 Å. We prefer to extend the coordination spheres to include anions at up to 3.617 Å from Te^{4+}. This yields Te^{4+} coordinations of 3 + 5 for both Te1 and Te2 and BVS of 4.11 and 4.14, respectively. Note that we have not included an O4 atom at a distance of 3.507 from Te1
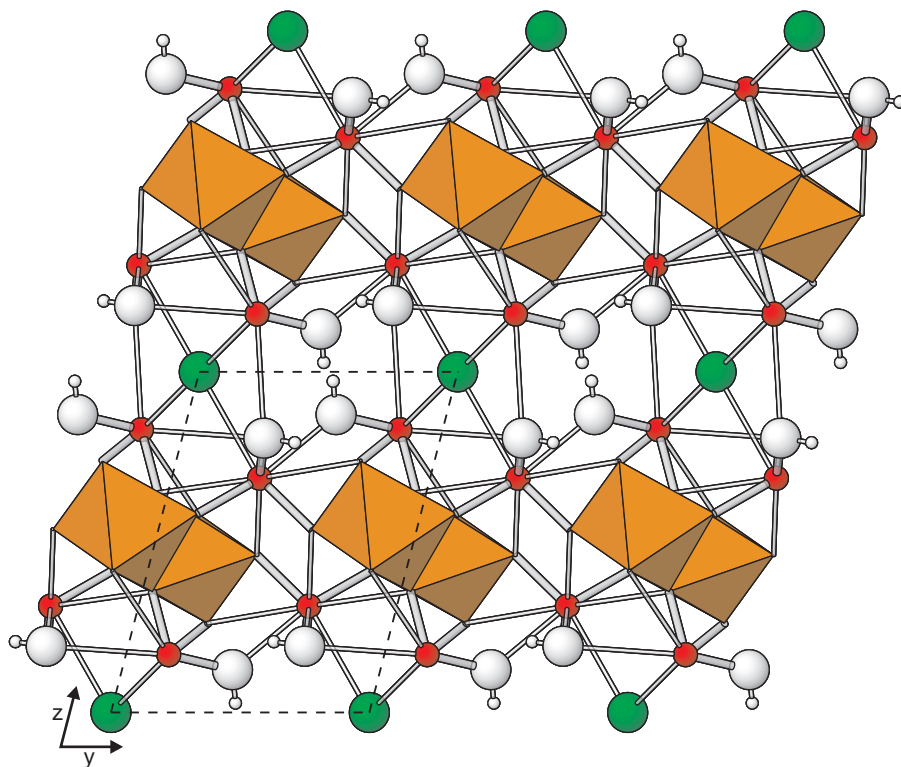
Fig. 3 Crystal structure of rodalquilarite along [001]. $Fe^{3+}O_6$ octahedra are shown in orange. Te atoms appear as red spheres, Cl atoms as green spheres, O atoms not in octahedra as large white spheres and H atoms as small white spheres. Short Te–O bonds of $Te^{4+}O_3$ pyramids are depicted as thick gray sticks.

because it is on the same side of the coordination as the three short Te1–O bonds. Even after extending the Te2 coordination to include the Cl at 3.479 Å, the BVS for Cl remains very low at 0.66 *vu*. This low BVS is probably a consequence of the Cl being placed on the center of symmetry at (0, 0, 0), where its bonds to the six surrounding Te^{4+} atoms are constrained to longer than normal lengths: 3.079 (×2), 3.112 (×2) and 3.479 (×2) Å. Similar situations in which an anion constrained to a special position is significantly over- or under-bonded to a cation with stereochemically active lone-pair electrons have been documented (e.g., Kampf et al. 2006; Fleet et al. 2010; Kampf and Housley 2011).

It is certainly noteworthy that the BVS for Te^{4+} in all three structures is significantly high, falling in the fairly narrow range 4.11 to 4.22 *vu*. We believe that this reflects a need to better determine the bond-valence parameters for Te^{4+}.

3.3. H atoms related to Te^{4+} coordinations

As noted above, Te^{4+} coordinations typically involve three short bonds to O atoms on the side of its coordination opposite to its lone-pair electrons, thereby forming a tightly bonded TeO_3 pyramid. The bond valence received by each of these O atoms in this pyramid is strongly dependent on the Te^{4+}–O bond length. For the shortest bonds, on the order of 1.82 Å, the O atoms receive a bond-valence contribution of about 1.5 *vu* from the Te^{4+}. The O atoms

participating in the longest of the short pyramidal bonds, on the order of 1.94 Å, receive as little as 1.1 *vu* from the Te^{4+}. Bond-valence balance dictates that none of the strongly bonded O atoms can be H_2O, but it is possible for them to be OH. In such a case, the OH attached to the Te^{4+} would generally not participate in any other bonds other than hydrogen bonds. Of course, the more distant O atoms may be either OH or H_2O.

Although juabite contains both OH and H_2O, neither participates in the Te^{4+} coordinations. The poughite structure contains H_2O, but no OH. The Te1 coordination in poughite includes one H_2O molecule, OW13 at a distance of 3.264 Å, and the Te2 coordination includes two H_2O molecules, OW2 and OW13 at 3.205 and 3.097 Å, respectively. The OW13 is shared between the two Te^{4+} coordinations and participates in no other bonds.

The rodalquilarite structure contains no H_2O molecules. Feger et al. (1999) reported both of the two nonequivalent H atoms in the structure to be bonded to O atoms in the $Te^{4+}O_3$ pyramids. They noted significant residual electron density at the 0; ½; 0 special position (center of symmetry), midway between two O6 atoms (which we refer to as OH6) at distances of 1.267 Å. Assuming this to be a H site, they postulated an unusual O–H–O linkage between two equivalent $Te^{4+}O_3$ pyramids. In our refinement, we did not detect any significant residual at (0, ½, 0). Rather, we noted a residual peak at (0.06, 0.47, 0.03), at a normal O–H distance of 0.90 Å from one OH6 and a normal H…O hydrogen bond dis-
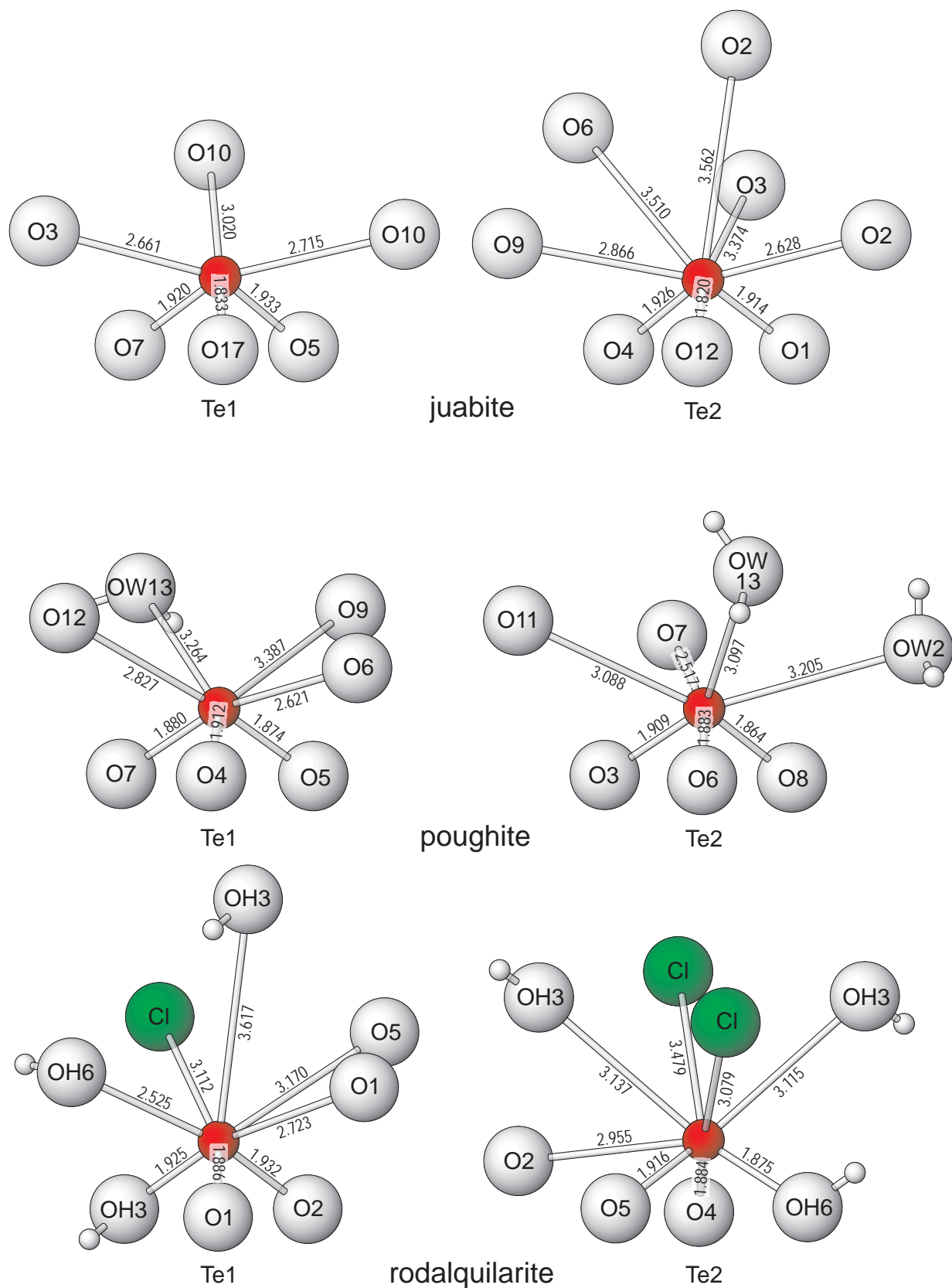
Fig. 4 Coordinations of Te atoms in juabite, poughite and rodalquilarite. The one-sided distributions of bond lengths are attributable to the localization of the 6s² lone-pair electrons, pointing approximately up in each case. Bond lengths are given in Å.
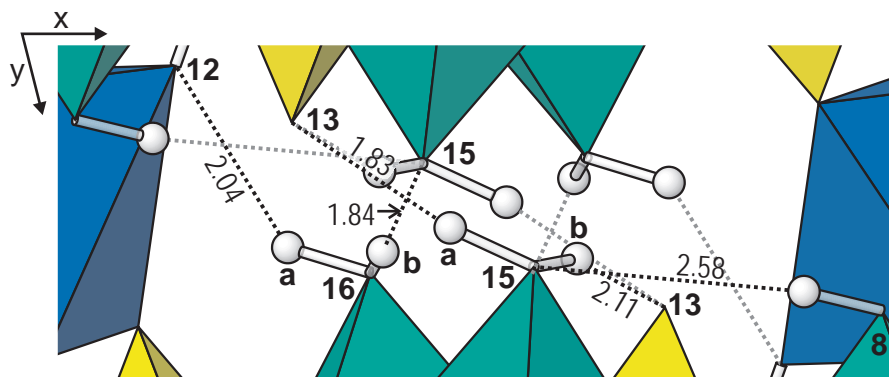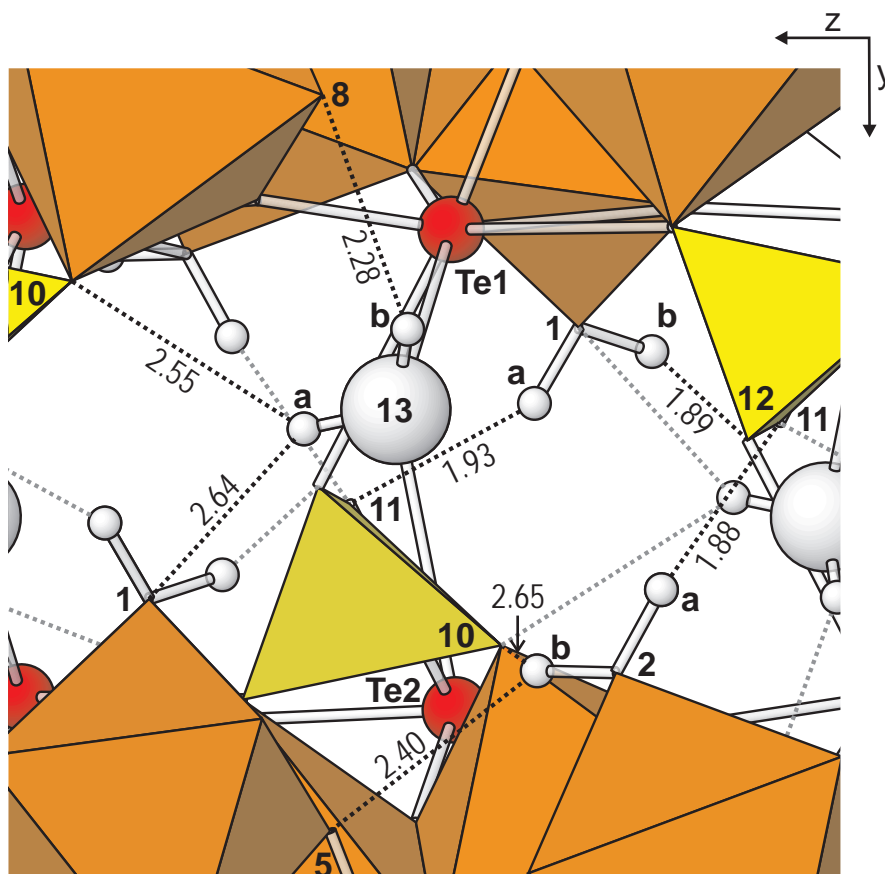
Fig. 5 Hydrogen bonding in juabite viewed along [001]. Oxygen atoms participating in hydrogen bonds are labelled with numbers and H atoms of H_2O molecules with letters (e.g. the O atom labelled "15" is OW15; the H atom noted with "a" and associated with OW15 is H15a). Bonds between H and acceptor O atoms are shown as dotted lines with distances in Å.

tance of 1.64 Å from the OH6 on the opposite side of the center of symmetry. The equivalent residuals on either side of the center of symmetry are only 0.81 Å apart, so we have interpreted this peak as a half-occupied H site and have refined it as such. The result is that each OH6 atom has one-half O and one-half OH character and the two equivalent Te2 pyramids are linked by the equivalent of one $(2 \times \frac{1}{2})$ hydrogen bond (see Fig. 7). In addition to participating in this hydrogen bond linkage between the Te2 pyramids, the OH6 also participates as one of the distant coordinating atoms to Te1, at a distance of 2.525 Å. The resulting BVS for OH6 is 2.05 *vu*. The Te1 pyramid in rodalquilarite also includes an OH group (OH3), but in this case the associated H site (H3) is fully occupied. Each OH3 also forms long bonds to two Te2 atoms at 3.115 and 3.137 Å. The resulting BVS for OH3 is also 2.05 *vu*.
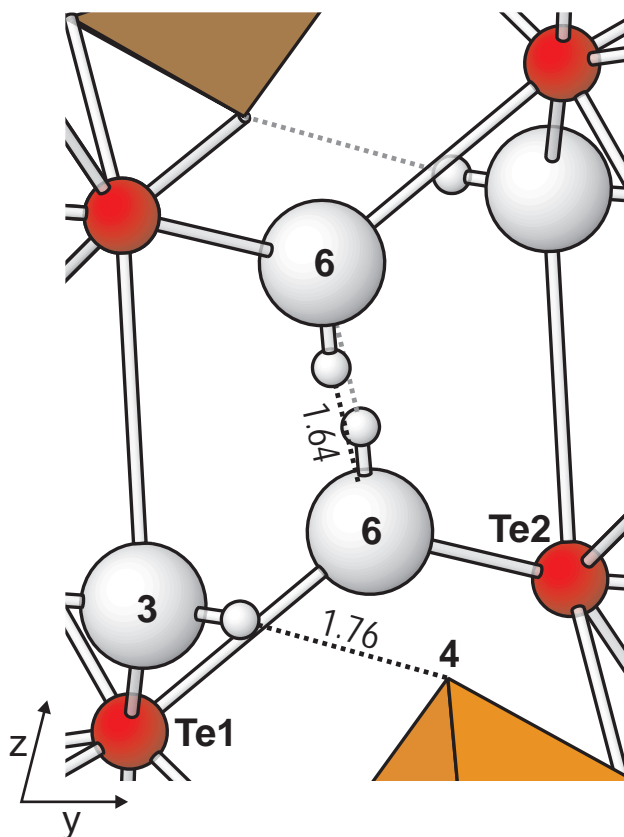
3.4. Hydrogen bonding

Burns et al. (2000) proposed a hydrogen bonding scheme for juabite. The H atom positions determined in our structure refinement confirm most of their proposed hydrogen bonds; however, while they did not assign any hydrogen bond from the H atom of the OH8, we have assigned a weak hydrogen bond to OW15.

Also, they assigned the hydrogen bonds from the OW15 H atoms to O13 and OW16, while we found that both OW15 H atoms form hydrogen bonds to O13. The bond distances and angles involved are listed in Tab. 3 and the complete hydrogen bonding scheme is shown in Fig. 5.

In the determination of the crystal structure of poughite, Pertlik (1971) did not propose a detailed hydrogen bonding scheme. The determination of H atom positions in our refinement coupled with the methods for bond-valence analysis have allowed us to provide a detailed description of the hydrogen bonding in the poughite structure. The bond distances and angles involved are listed in Tab. 3 and the bonding is shown in Fig. 6. The H

Fig. 6 Hydrogen bonding in poughite viewed along [100]. Oxygen atoms participating in hydrogen bonds are labelled with numbers and H atoms with letters (e.g. the O atom labelled "1" is OW1; the H atom noted with "a" and associated with OW1 is H1a). Bonds between H and acceptor O atoms are shown as dotted lines with distances in Å.

Fig. 7 Hydrogen bonding in rodalquilarite viewed along [Ī00]. Oxygen atoms participating in hydrogen bonds are labelled with numbers, e.g. the O atom labelled "3" is O3 and the H atom associated with O3 is H3. Bonds between H and acceptor O atoms are shown as dotted lines with distances in Å. Note that locally only one of the two shown H6 atoms is present.

atoms associated with OW1, H1a and H1b, form a single hydrogen bond to O11 and O12, respectively. The H2a atom of the OW2 molecule also forms a single hydrogen bond to O11, while the H2b atom forms bifurcated hydrogen bonds to O5 and O10. The H13a atom of the OW13 molecule forms bifurcated hydrogen bonds to O10 and OW1 and the H13b atom form a single hydrogen bond to O8.

As stated above, Feger et al. (1999) noted a H site on the center of symmetry at (0, ½, 0) between two O6 atoms at a distance of 1.267 Å from each and forming an unusual O–H–O linkage. Our refinement does not support this. Instead, we have determined there to be a half-occupied H atom site, just off the center of symmetry. The effective result is a normal hydrogen bond between O6 (which we refer to as OH6) atoms on either side of the center of symmetry. The H atom (H3) bonded to O3 (which we refer to as OH3) was not assigned a hydrogen bond by Feger et al. (1999). We note that H3 forms a hydrogen bond to O4 at a distance of 1.76 Å. This bond contributes significantly to the BVS of O4. We have ob-

tained a BVS for O4 of 2.11 *vu*, while Feger et al. (1999), clearly neglecting the hydrogen bond, reported 1.91 *vu*. The bond distances and angles involved are listed in Tab. 3 and the bonding is shown in Fig. 7.

4. Conclusions

The Te^{4+} (tellurite) cation typically forms one-sided coordinations to O atoms, attributable to its stereochemically active $6s^2$ lone-electron-pair. For Te^{4+} phases that also contain H, the determination of the H atom positions can be essential in confirming the assignments of hydrogen bonds, which significantly contribute to the bond-valence balance. In turn, bond-valence analysis is useful in understanding the role of H atoms in Te^{4+} coordinations, and for understanding the linkages within the structure as a whole. The structures of juabite, poughite and rodalquilarite have overall linkage schemes that are quite different, yet all can be considered layer structures in which relatively weak long Te–O and/or Te–Cl bonds are involved in the linkages between layers. In juabite, a long apical Cu–O bond participates in the linkage between layers and, in poughite and rodalquilarite, hydrogen bonding also links the layers.

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