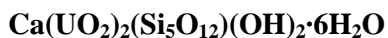


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Revision II

Revision of the crystal structure and chemical formula of haiweeite,



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ABSTRACT

The previously published crystal structure study suggested that haiweeite is orthorhombic, *Cmcm*, with $a = 7.125(1)$, $b = 17.937(2)$, $c = 18.342(2)$ Å and $V = 2344.3(7)$ Å³, and an ideal chemical formula $\text{Ca}[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2] \cdot 3\text{H}_2\text{O}$, with $Z = 4$. Using single-crystal X-ray diffraction and electron microprobe analysis we re-examined haiweeite from the Teofilo Otoni, Minas Gerais, Brazil. Our diffraction experiment provided weak reflections responsible for doubling of the b cell parameter (for the current space-group settings), leading finally to the choice of a different space group. Haiweeite is thus orthorhombic, the space group *Pbcn*, with the unit cell parameters $a = 18.3000(5)$, $b = 14.2331(3)$, $c = 17.9192(5)$ Å, $V = 4667.3(2)$ Å³, and an ideal formula $\text{Ca}[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2(\text{Si}_3\text{O}_6)] \cdot 6\text{H}_2\text{O}$ (6.25 H₂O inferred from the thermal analysis; 7.50 H₂O from the structure model), with $Z = 8$. The structure refinement yielded $R_{\text{obs}} = 0.0512$ for 2498 observed reflections [$I_{\text{obs}} > 3\sigma(I)$] and $R_{\text{all}} = 0.1286$ for all 6117 unique reflections. Structure solution confirmed by refinement provided a structure model with full occupancies for U, Si and Ca atoms, contrasting to previous average structure model. Although the general topology of our structure resembles that

28 reported previously, all Si and O sites in our structure are fully occupied, in contrast to the
29 previous structure determination.

30

31 **Keywords:** haiweeite, uranyl silicate, sheets of polyhedra, crystal structure, X-ray diffraction
32

33 **Running title:** The revision of haiweeite

34

35

INTRODUCTION

36 Haiweeite was firstly found in 1959 at Coso Mountains, California, near the Haiwee
37 Reservoir and described as a new mineral species by McBurney and Murdoch (1959). They
38 ascribed a chemical formula $\text{Ca}(\text{UO}_2)_2\text{Si}_6\text{O}_{15}\cdot 5\text{H}_2\text{O}$, $Z = 2$, to it. Based on Weissenberg
39 photographs they inferred haiweeite to be probably monoclinic, with the space group $P2/c$,
40 and unit-cell parameters $a = 15.4$, $b = 7.05$, $c = 7.10 \text{ \AA}$ and $\beta = 107.52^\circ$. Since that find,
41 haiweeite has been found on many localities in the world. Namely, exceptional specimens of
42 haiweeite originate from Brazil pegmatite localities, such as Minas Gerais or São Paulo. First
43 structure determination was done by Rastsvetaeva et al. (1997) using X-ray single-crystal
44 diffraction data on a twinned microcrystal. The reported crystal structure involved a new type
45 of sheet of uranyl pentagonal bipyramids and silicate tetrahedra. However, their model could
46 not be fully refined resulted in R -factor of 11.8% (using the space group $P2_12_12_1$) and unit
47 cell dimensions $a = 14.263(3)$, $b = 17.988(3)$, $c = 18.395(3) \text{ \AA}$. Later, Burns (2001) reported a
48 full structure determination for a haiweeite crystal from Teofilo Otoni, Minas Gerais, Brazil.
49 The crystal structure was refined to $R_1 = 4.2\%$ for 1181 unique observed reflections [$|F_o| \leq$
50 $4\sigma(F)$], for orthorhombic $Cmcm$ space group, with $a = 7.125(1)$, $b = 17.937(2)$, $c = 18.342(2)$
51 \AA and $V = 2344.3(7) \text{ \AA}^3$ with $Z = 4$, and resulted in structure formula
52 $\text{Ca}[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2](\text{H}_2\text{O})_3$. Despite of the lower R -factor and at the first glance
53 reasonable structure solution, the crystal structure contains few peculiar features similar to

54 those reported by Jackson and Burns (2001) for weeksite, which has been later revisited by
55 Fejfarová et al. (2012). Crystal structure of haiweeite provided by Burns (2001) contains few
56 Si and O sites, which are populated by 50% and 25%, respectively, indicating that the model
57 is actually just a representation of an average structure. Also the coordination of the Ca atom
58 yielded a strongly distorted octahedron, which is less usual in the oxysalts containing Ca²⁺.
59 Our study presents a novel determination of the haiweeite structure from single-crystal X-ray
60 diffraction data. The refinement of the crystal structure of haiweeite was performed for the
61 orthorhombic space group *Pbcn*.

62

63

EXPERIMENTAL METHODS

64

The haiweeite sample used in this study originates from the Teofilo Ottoni, Minas Gerais, Brazil. Its
65 chemical composition (Table 1) was analyzed using a Cameca SX100 electron microprobe at Masaryk
66 University, Brno, with an operating voltage of 15 kV, 10 nA current, and 8 μm beam diameter. The following
67 X-ray lines, crystals, and standards were selected to minimize line overlap: *Kα* lines: Si (TAP, titanite), Ca
68 (PET, titanite), K (PET, sanidine); and *Mβ* lines: U (LPET, U metal). Peak counting times were 10–20 s for
69 major elements and 40–60 s for minor or trace elements. Counting time on background was half of peak
70 counting times. The measured intensities were converted to element concentrations using the “X-PHI”
71 correction routine (Merlet 1994). Thermal analysis (TGA) of haiweeite was performed on Stanton–Redcroft
72 Thermobalance 750 using a sample of the weight 3.937 mg, heating rate 10 °C/min and a dynamic air
73 atmosphere (10 ml/min).

74

The long prismatic haiweeite crystal, of the yellow color, having dimensions 0.352 × 0.049 × 0.023
75 mm³, was selected and examined using an Oxford Diffraction Gemini single-crystal diffractometer equipped
76 with the Atlas CCD detector and a monochromated MoK α radiation from the sealed X-ray tube, collimated with
77 fibre-optics Mo-Enhance collimator. Pre-experiments provided similar unit-cell parameters matching those
78 reported by Burns (2001), however by careful inspection of the frames, the weak additional reflections were
79 found, therefore an extended exposure (2×100 sec per °) was set during the full data collection. These reflections
80 were found to be responsible for a doubling of the *a* parameter (the total of 4462 observed measured reflections
81 with average *I*/ $\sigma(I)$ = 1.15). The refined unit cell parameters are: *a* = 14.2331(3), *b* = 17.9192(5), *c* = 18.3000(5)

82 Å, with $V = 4667.3(2) \text{ \AA}^3$. Along with the reflections responsible for doubling of the unit cell volume, additional
83 weak reflections were found on the frames. Analysis showed, that these weak reflections might adhere to the
84 split crystals. The twinning matrices describing four twin domains were introduced into the later refinement,
85 however, they were not followed by the better R -factor and did not affect the difference Fourier maxima /see
86 below/. Finally, diffuse scattering effects (as streaking of some reflections) appeared at the diffraction frames.
87 They might be connected with some short-range ordering of e.g. Ca atoms. An empirical absorption correction
88 applied during the data reduction using the program CrysAlis (multi-scan in ABSPACK3, CrysAlis RED,
89 Agilent Technologies 2010) led to the internal R -factor 0.0749 for orthorhombic mmm Laue symmetry.
90 Structure was solved using the charge-flipping algorithm of the Superflip program (Palatinus and Chapuis
91 2007). Based on reflections conditions P cell was chosen leading to the orthorhombic unit cell $Pbna$, which was
92 further transformed to the standard setting of the space group $Pbcn$. For the structure refinement software
93 JANA2006 (Petříček et al. 2006) was utilized. Details of the data collection and the structure refinement are
94 listed in Table 2. The refinement of the structure proved that in the chosen space group, different from that
95 proposed by Burns (2001), all problematic disorders on SiO_4 tetrahedra disappear. During the structure
96 refinements U, Si and Ca sites were assumed to be fully occupied, as indicated by the chemical analysis and
97 later confirmed by the refinement. Occupation factor of the O25 was set to 25% (50% of its refined occupancy)
98 due to the fact that the separation distance to the symmetrically equivalent position is low ($\sim 2.4 \text{ \AA}$). Final
99 refinement provided very prolate ADP ellipsoids for atoms O20, O21, O24 and O26; they were treated as split
100 into the two positions (O20 and O20', O21 and O21', O24 and O24', O25 and O25', O26 and O26'). Except
101 O26 and O26' atoms, each pair has 50% occupancy and was refined with isotropic displacement parameters.
102 The refinement, based on F^2 , converged with the final $R_{\text{obs}} = 0.0512$, $wR_{\text{obs}} = 0.1221$ and GOF (obs) = 1.84 for
103 2498 observed [$I_{\text{obs}} > 3\sigma(I)$]. Final atomic coordinates and displacement parameters are given in Table 3 and
104 selected bond distances in Table 4. The final difference Fourier analysis provided quite high values of 9.70 e\AA^{-3}
105 /with the two highest peaks located very close, 0.21 \AA , to both U1 and U2 atoms however, with a very small
106 charge – the highest has 0.270/. We found, that introducing the twins (belonging to the split crystals) into the
107 refinement, lead neither to a better fit to the data, nor to the vanishing of spurious Fourier peaks. Moreover, we
108 suppose, that these maxima are connected with Fourier synthesis artifacts, because they are present in F_{calc}
109 (checking Fourier) maps at the same position as in the difference Fourier maps. When modeling the calculated
110 structure from the data to high diffraction vectors, the highest maxima disappear then.

111

112

RESULTS

113 *WDS study and thermal analysis*

114 The accepted chemical formula of haiweeite in the current IMA mineral list is
115 $\text{Ca}(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, based on the structure given by Burns (2001). However, current
116 structure refinement indicated that the studied crystal contains more H_2O than previously
117 reported (see below). The chemical composition of the studied haiweeite crystal (Table 1) can
118 be expressed by the empirical formula $(\text{Ca}_{1.01}\text{K}_{0.02})_{1.03}[(\text{UO}_2)_{2.00}\text{Si}_{4.99}\text{O}_{12}(\text{OH})_2] \cdot 6.28\text{H}_2\text{O}$ (see
119 the thermal analysis), or simplified as $\text{Ca}(\text{UO}_2)_2(\text{Si}_5\text{O}_{12})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$. The major difference
120 between the two simplified formulas lies in the H_2O content.

121 Haiweeite dehydrates and dehydroxylates in four partly overlapping steps: 1) release
122 of 2.81 H_2O (4.75 wt% up to 88 °C); 2) 1.05 H_2O (1.78 wt% to 133 °C); 3) 1.20 H_2O (2.03
123 wt% 38 °C), 4) 2.22 $\text{H}_2\text{O} = 1.22 \text{H}_2\text{O} + 2 \text{OH}$ (3.76 wt% to 614 °C). They are followed by
124 release of some oxygen (0.51 wt% which corresponds to $\sim 0.19 \text{O}_2$) from formation of
125 calcium diuranate (up to 900 °C). The total weight loss from the TG is 12.83 wt%, which
126 corresponds to the sum of 7.28 H_2O (including $\sim 2 \text{OH}$ groups) and $\sim 0.19 \text{O}_2$. Endproducts of
127 the thermal decomposition are CaU_2O_7 and amorphous SiO_2 . The difference between
128 expected theoretical content of water molecules and hydroxyl groups (theoretical molecular
129 weight of haiweeite containing 3 $\text{H}_2\text{O} + 2 \text{OH}$ is 1000.633) and that experimentally observed
130 (molecular weight of haiweeite studied is 1065.207) prove that studied haiweeite contains
131 more H_2O than was accepted before, i.e. approximately 7.28 H_2O .

132

133 *Crystal structure*

134 The basic features of the haiweeite structure determined from this study are quite
135 similar to those reported by Burns (2001). There are two symmetrically distinct U^{6+} sites,
136 coordinated by two strongly bonded O atoms to form UO_2^{2+} and additionally by five O atoms

137 arranged at the equatorial vertices of pentagonal bipyramid. The $(\text{UO}_2)\text{O}_5$ pentagonal
138 bipyramids share equatorial edges to form chains parallel to $[010]$, which in turn share edges
139 with SiO_4 tetrahedra (staggered along the chain length). Adjacent chains of uranyl polyhedra
140 and silicate tetrahedra are cross linked forming sheets parallel to (001) by sharing corners
141 with the Si_3 and Si_4 tetrahedra (Fig. 1). The Si_1 , Si_2 , Si_3 and Si_5 tetrahedra share vertices,
142 forming four-membered rings, with linkage between the rings provided by the vertex sharing
143 with the Si_4 tetrahedron (Fig. 1). Two of the tetrahedra contain protonated oxygen atoms O6
144 (Si_3) and O10 (Si_5) as is indicated by the bond-valence analysis (Table 5).

145 In the structure of haiweeite, there is one unique Ca atom, $[8]$ -coordinated as a
146 distorted square antiprism by O atoms and H_2O (when considering unsplit O sites). Ca-
147 polyhedra share edges forming dimers of the composition $\text{Ca}_2(\text{O}_{\text{Ur}2})_2(\text{H}_2\text{O})_{12}$ in the interlayer
148 (Fig. 2). The adjacent uranyl silicate sheets are linked through the dimers of Ca-polyhedra,
149 where O7 (Ur) is coordinated to both the sheet and Ca atom. In the structure there are twelve
150 O positions (including five split-sites) adhering to the molecular H_2O (Table 5), three of them
151 (1+1 split site) are not coordinated to any cation and holds in the structure only by hydrogen
152 bonds as indicated by the bond-valence analysis (Table 5). The O...O separation distances
153 found in the structure (Table 4) are quite characteristic for hydrous species bonded by
154 hydrogen bonds. The H-atoms belonging to OH groups, which were not determined by the
155 current refinement, are located at the apical oxygen atoms O6 and O10 (Table 5), which are
156 oriented towards the interlayer (Fig. 2).

157 Experimental structural formula of haiweeite obtained from the refinement and bond-
158 valence analysis (Table 5) is $^{[8]}\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2(\text{Si}_3\text{O}_6)(\text{H}_2\text{O})_{7.5}$, $Z = 8$.

159

160

DISCUSSION

161 Crystal structure of haiweeite is built upon sheets of uranyl pentagonal bipyramids and

162 silicate tetrahedra, which are topologically different from uranophane group of minerals
163 (Burns 2001, 2005), due to a different way of linkage between uranyl bipyramids and
164 tetrahedral units. The structural sheets found in haiweeite are topologically identical to those
165 found in weeksite (Burns 2005; Fejfarová et al. 2012), but in latter, sheets are connected to
166 form a framework due to the sharing of oxygen atoms at the vertices of silicate tetrahedra.

167 Despite of general similarities between current structure determination and structure
168 provided by Burns (2001), there are some significant differences. As was mentioned in the
169 introduction, previous structure determination identified few atomic sites /Si(3), Si(4) and
170 O(6), O(8), O(9), OH(10), H₂O(11), H₂O(12), H₂O(13); labeling is after Burns 2001/, which
171 are 50% or 25% occupied. Burns (2001) noticed, that there was no evidence for twinning in
172 the structure, and he commented the model to be representation of an average structure. By
173 the current study we found the *b* cell parameter to be doubled, with the weak reflections
174 responsible for that. Burns (2001) noted that the crystal was checked for doubling the
175 corresponding unit cell parameter (parameter *a* in that case) using an APEX detector. Though
176 careful inspection no significant reflections were observed that would require the doubling of
177 the one parameter. The crystal used by Burns (2001) for the structure determination was
178 considerably smaller (about six times in crystal volume) than the one used in the current
179 study. We consider that this may be the reason why the weak reflections were not observed
180 by the previous study.

181 Our choice of the unit cell is similar to that of Rastsvetaeva et al. (1997), however,
182 based on reflection conditions the different orthorhombic space group was chosen. The
183 refinement of the current structure model provided full site-occupancies for all atomic sites,
184 which were described by Burns (2001) as disordered with lowered occupancies, except these
185 belonging to molecular H₂O. The current solution provided coordination of Ca²⁺ in the
186 interlayer as distorted [8]-fold coordination polyhedra, forming dimers, compared to the

187 previous model, possessing strongly distorted octahedron. This is reflected in different
188 number of water molecules coordinated to Ca^{2+} . In the case of the current study, we inferred
189 6.28 H_2O from thermal analysis and 7.50 H_2O corresponding to the O sites belonging to
190 hydrous species in the structure model. Due to the fact, that refinement of occupational
191 factors for O atoms in presence of heavy-scattering U atoms (and only poor absorption
192 correction) may provide misleading results, the site occupancies for O atoms of the H_2O
193 groups were not refined. The question of possible variability in H_2O content remains open as
194 well as the related issue concerning the stability of such structures. It is also possible, that
195 haiweeite structure can possess [6]-coordinated Ca, with 3 H_2O in the interlayer and with same
196 composition of the sheets as in case of current study. Let's try to elucidate these questions
197 using simple considerations resulting from the bond-valence approach (according to
198 Schindler and Hawthorne 2008).

199 Structural sheets in haiweeite of the composition $[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2]^{2-}$ found by
200 Burns (2001) and confirmed by current study, are characterized by *CDA* (charge deficiency
201 per anion) value of 0.13 *vu*. The Lewis basicity characteristic for the sheet of such
202 composition was calculated to be in the range 0.13–0.24 *vu*; this value is similar to the
203 uranophane group of minerals (0.15–0.25 *vu*) and to kasolite (0.19–0.25 *vu*) (Schindler and
204 Hawthorne 2008). Corresponding Lewis acidity of the interstitial complex in haiweeite, while
205 calculating [8]-Ca and seven H_2O , is 0.16 *vu*, thus within the range of Lewis basicity of the
206 structure sheets. In that case all transformer (H_2O) groups are considered to be fully occupied,
207 in the reality value of the Lewis acidity will be higher. The bond-valence distribution factor
208 *D*, which is the ratio between the number of anions in the structural unit and the number of
209 bonds emanating from interstitial cations plus OH groups of the structural unit, determines
210 the number and the type of H_2O groups in the interstitial species (Schindler and Hawthorne
211 2008). Consequently, this parameter can be used as a measure of degree of polymerization of

212 the structural units, because less polymerized sheets (lower density of bond-valence
213 acceptors) contain fewer H₂O in interlayer and vice versa (Schindler and Hawthorne 2008).
214 Note that e.g., number of OH at the structural unit and number of bonds from interstitial are
215 not mutually independent values. The factor *D* was used by Schindler and Hawthorne (2008)
216 to predict total number of H₂O and also number of transformer H₂O groups in the interlayer.
217 Calculated values of *D*, total number of predicted H₂O, number of predicted transformer H₂O
218 and number of observed H₂O for haiweeite and other uranyl silicates are given in Table 6. We
219 can read out from the table that with increasing *D*, as the measure of the polymerization of the
220 sheets, the H₂O content (either calculated or observed) in the interlayer also increases. The
221 Ca²⁺ cation in solids usually has the coordination number of [6], [7] or [8]. Burns (2001)
222 reported that Ca²⁺ in haiweeite has a distorted octahedral coordination. In such case,
223 according to BV calculations, there should be in total nine H₂O (including at least five
224 transformer H₂O) to transfer bond-valence from interstitial to acceptors in the structure
225 sheets. Burns (2001) gave sum of three H₂O based on the refinement. In case that all of these
226 three (H₂O) will be transformer groups, resulting in six bonds from H atoms to the acceptors,
227 still at least two transformer (H₂O) groups will be needed in order to mediate bond-valence
228 from cations to anions. These H₂O groups are missing in the model of Burns (2001).
229 Conversely, calculations based on the current structure determination, which provided Ca²⁺ in
230 a distorted [8]-fold coordination, suggest that six H₂O should be present, three transformer
231 groups and three non- or inverse-transformer H₂O. Current structure model involves seven O
232 sites, where two shared oxygen atoms (O18) belong to non-transformer H₂^[4]O, five
233 remaining sites to transformer and non-transformer H₂O. The decrease of H₂O content, and
234 thus some restricted variability in it, may be possible for haiweeite, but if so, it should be
235 connected to some change in the composition of the sheets, especially in the OH content.
236

237

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REFERENCES CITED

- 248 Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta*
249 *Crystallographica*, B47, 192–197.
- 250 Brown, I.D., and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic
251 analysis of the inorganic crystal structure database. *Acta Crystallographica*, B41, 244–
252 248.
- 253 Burns, P.C. (1998) The structure of boltwoodite and implications of solid solution toward
254 sodium boltwoodite. *Canadian Mineralogist*, 36, 1069–1075.
- 255 Burns, P.C. (2001) A new uranyl silicate sheet in the structure of haiweeite and comparison
256 with other uranyl silicates. *Canadian Mineralogist*, 39, 1153–1160.
- 257 Burns, P.C. (2005) U⁶⁺ minerals and inorganic compounds: insights into an expanded
258 structural hierarchy of crystal structures. *Canadian Mineralogist*, 43, 1839–1894.
- 259 Burns, P.C., Ewing, R.C., and Hawthorne, F.C. (1997) The crystal chemistry of hexavalent
260 uranium: polyhedron geometries, bond-valence parameters, and polymerization of
261 polyhedra. *Canadian Mineralogist*, 35, 1551–1570.
- 262 Demartin, F., Gramaccioli, C.M., and Pilati, T. (1992) The importance of accurate crystal
263 structure determination of uranium minerals. II. Soddyite (UO₂)₂(SiO₄)·2H₂O. *Acta*
264 *Crystallographica*, C48, 1–4.
- 265 Fejfarová, K., Dušek, M., Plášil, J., Čejka, J., Sejkora, J., Škoda, R. (2011) Reinvestigation of
266 the crystal structure of kasolite, Pb[(UO₂)(SiO₄)](H₂O), an important alteration product
267 of uraninite, UO_{2+x}. *Journal of Nuclear Materials*, *in press*,
268 <http://dx.doi.org/10.1016/j.jnucmat.2010.11.064>.
- 269 Fejfarová, K., Plášil, J., Yang, H., Čejka, J., Dušek, M., Downs, R.T., Barkley, M.C., and
270 Škoda, R. (2012) Revision of the crystal structure and chemical formula of weeksite,
271 K₂(UO₂)₂(Si₅O₁₃)·4H₂O. *American Mineralogist*, 97, 750–754.
- 272 Ginderow, D. (1988) Structure de l'uranophane alpha, Ca(UO₂)₂(SiO₃OH)₂·5H₂O. *Acta*
273 *Crystallographica*, C44, 421–424.

- 274 Jackson, J.M., and Burns, P.C. (2001) A re-evaluation of the structure of weeksite, a uranyl
275 silicate framework mineral. *Canadian Mineralogist*, 39, 187–195.
- 276 Kubatko, K.A., and Burns, P.C. (2006) A novel arrangement of silicate tetrahedra in the
277 uranyl silicate sheet of oursinite, $(\text{Co}_{0.8}\text{Mg}_{0.2})[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_6$. *American*
278 *Mineralogist*, 91, 333–336.
- 279 McBurney, T.C., and Murdoch, J. (1959) Haiweeite, a new uranium mineral from California.
280 *American Mineralogist*, 44, 839–843.
- 281 Merlet, C. (1994) An accurate computer correction program for quantitative electron-probe
282 microanalysis. *Microchimica Acta*, 114, 363–376.
- 283 Palatinus, L., and Chapuis, G. (2007) Superflip – a computer program for the solution of
284 crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied*
285 *Crystallography*, 40, 451–456.
- 286 Petříček, V., Dušek, M., and Palatinus, L. (2006) Jana2006. The crystallographic computing
287 system. Institute of Physics, Praha, Czech Republic. can be obtained from
288 <http://jana.fzu.cz>
- 289 Rastsvetaeva, R.K., Arakcheeva, A.V., Pushcharovsky, D.Yu., Atencio, D., and Menezes
290 Filho, L.A.D. (1997) A new silicon band in the haiweete [sic] structure. *Crystallography*
291 *Reports*, 42, 927–933.
- 292 Rosenzweig, A., and Ryan, R.R. (1975) Refinement of the crystal structure of
293 cuprosklodowskite $\text{Cu}[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2] \cdot 6\text{H}_2\text{O}$. *American Mineralogist*, 60, 448–453.
- 294 Ryan, R.R., and Rosenzweig, A. (1977) Sklodowskite, $\text{MgO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 7\text{H}_2\text{O}$. *Crystal*
295 *Structure Communications*, 6, 611–615.
- 296 Schindler, M., and Hawthorne, F.C. (2008) The stereochemistry and chemical composition of
297 interstitial complexes in uranyl-oxysalt minerals. *Canadian Mineralogist*, 46, 467–501.

298

299 List of Tables

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303 haiweeite.

304 Table 4. Selected bond distances for the structure of haiweeite.

305 Table 5. Bond-valence analysis for haiweeite.

306 Table 6. Values of the bond-valence distribution factor D and the number of predicted and
307 observed H_2O for uranyl silicate minerals based on the bond-valence approach.

308

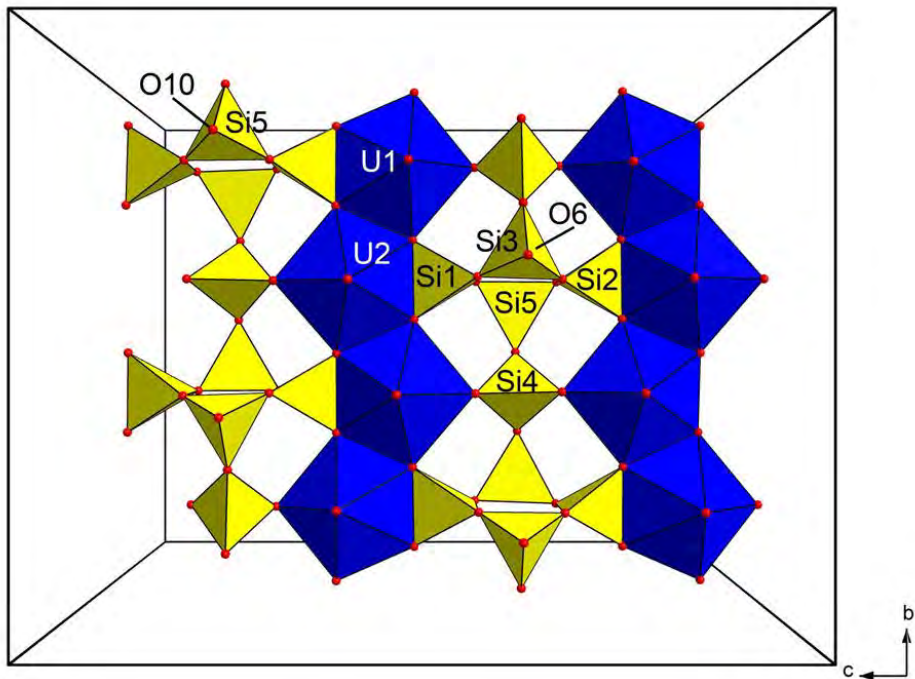
309 List of Figure Captions

310 FIGURE 1 Uranyl silicate sheets in the crystal structure of haiweeite. Uranyl pentagonal
311 bipyramids (blue) extending along [100] and of chains of silicate tetrahedra are linked
312 together by sharing of vertices and an edge between uranyl bipyramid and Si1 and Si2
313 tetrahedra.

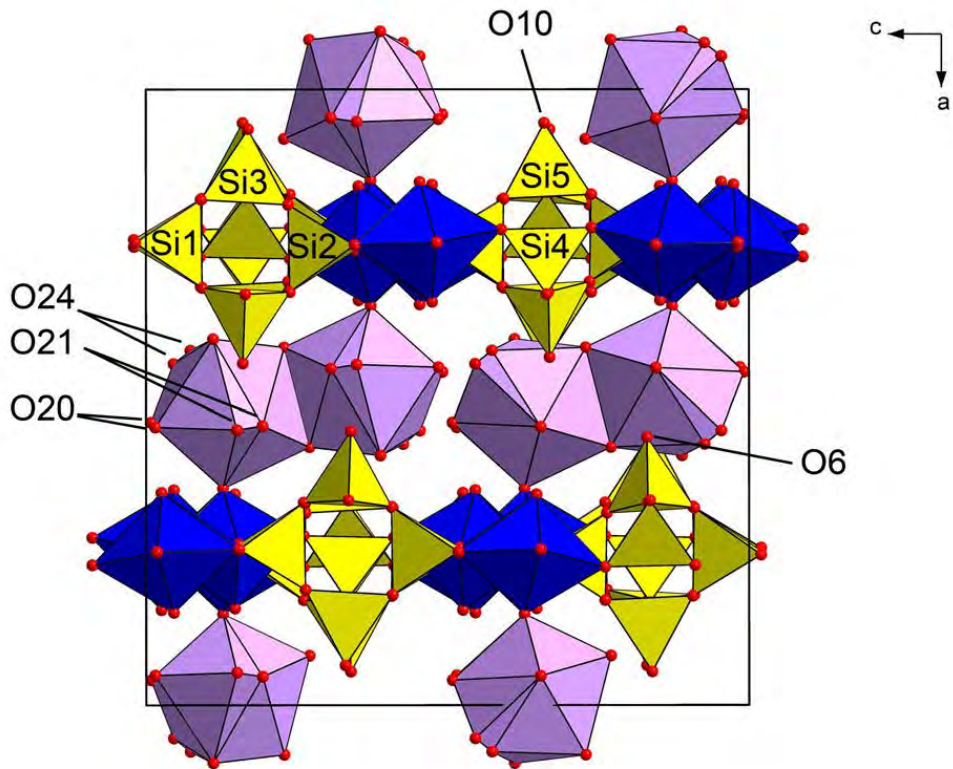
314

315 FIGURE 2. Crystal structure of haiweeite in the view along [010]. Adjacent sheets of uranyl
316 pentagonal bipyramids and silicate chains (labeled) are linked through the sharing of dimers
317 of Ca-polyhedra (purple) in interlayer. Labeled are atoms belonging to OH groups (O6, O10)
318 and split-sites of the (H_2O) groups (O20, O21, O24). Else (H_2O) non-bonded to any
319 interstitial cation were omitted for clarity. Unit-cell edges are outlined by thick solid black
320 line.

321



1



Tables

TABLE 1. Results of electron microprobe analyses (in wt%) of haiweeite

Constituent	This work				McBurney and Murdoch (1959) [§]
	Mean	Range	St.dev.	Det. lim.	
K ₂ O	0.11	0.04–0.22	0.05	0.05	–
CaO	5.72	5.59–5.87	0.09	0.01	5.4
SiO ₂	30.34	29.78–30.89	0.37	0.05	33.1
UO ₃	58.01	57.34–59.55	0.76	0.30	52.8
H ₂ O*	13.19				8.7
Total	107.38 [#]	93.61–95.74			100.0
K	0.023				–
Ca	1.005				1.0
ΣM site	1.028				1.0
Si ⁴⁺	4.974				6.0
UO ₂	1.998				2.0
H ₂ O+OH	7.212				5.2

Mean – Mean of 6 representative analyses; coefficients of the empirical formula were calculated on the basis of (Si+U+K+Ca) = 8 O
apfu

Range – Range of 6 representative analyses

St.dev. – Standard deviation of the 6 analyses (in wt%)

Det. lim. – detection limit (in wt%)

H₂O* – Water content (in wt%) derived from the content of 7.28 H₂O (H₂O+OH) inferred from the thermal analysis of haiweeite

– High total affected by the uneven surface of the polished section, partial loss of molecular water under the vacuum and a beam-damage during analysis

\$ – Empirical formula calculated on the basis of 9 *apfu* reported in the primary reference

TABLE 2. Summary of data collection conditions and refinement parameters for haiweeite

Crystal data	
Structural formula	Ca(UO ₂) ₂ (Si ₅ O ₁₂)(OH) ₂ ·7.5H ₂ O
Space group	<i>Pbcn</i>
<i>a</i> (Å)	18.3000(5)
<i>b</i> (Å)	14.2331(3)
<i>c</i> (Å)	17.9192(5)
<i>V</i> (Å ³)	4667.3(2)
<i>Z</i>	8
Calculated density (g/cm ³)	3.08
μ (mm ⁻¹), correction type	14.42, multi-scan
T_{\min}/T_{\max}	0.6799/1.0000
Crystal size (mm)	0.352×0.049×0.023
Data collection	
Radiation, wavelength (Å)	MoK α , 0.71073
θ range for data collection (°)	2.857 – 29.356
<i>h</i> , <i>k</i> , <i>l</i> ranges	-25< <i>h</i> <23, -18< <i>k</i> <19, -23< <i>l</i> <24,
Axis, frame width (°), time per frame (s)	ω , 1.0, 100
Total reflections collected	71814
Unique reflections	6117
Unique observed reflections [<i>I</i> _{obs} >3 σ (<i>I</i>)]	2498
Data completeness to θ_{\max} (%), <i>R</i> _{int}	99.75, 0.0749
Structure refinement by JANA2006	
Refinement method	Full-matrix least-squares on <i>F</i> ²
No. parameters, constraints, restraints	189, 5, 0
Weighting details	σ , $w = 1/(\sigma^2(I) + 0.0016I^2)$
<i>R</i> ₁ , <i>wR</i> ₂ (obs)	0.0512, 0.1221
<i>R</i> ₁ , <i>wR</i> ₂ (all)	0.1286, 0.1505
GOF on <i>F</i> ² _{obs} /on <i>F</i> ² _{all}	1.84/1.42
Largest diff. peak and hole (e/Å ³)	9.70, -3.56

TABLE 3. Atomic coordinates, site occupancies and atomic displacement parameters (in Å²) for haiweeite.

Atom	x	y	z	U_{eq}/U_{iso}^*	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.24799(2)	0.12566(5)	0.034427(19)	0.01044(12)	0.0202(2)	0.00590(19)	0.00521(19)	0.00036(17)	-0.00001(18)	-0.0003(4)
U2	0.25411(2)	0.37558(6)	0.13863(2)	0.00964(12)	0.0174(2)	0.00550(19)	0.0060(2)	0.00020(17)	0.00013(17)	-0.0006(4)
Ca	0.01502(16)	0.8775(2)	0.13941(17)	0.0328(9)	0.0235(14)	0.0358(16)	0.0391(16)	-0.0045(15)	0.0043(12)	-0.0085(18)
Si1	0.24794(18)	0.3757(4)	-0.03695(15)	0.0120(9)	0.0249(18)	0.0058(13)	0.0053(13)	0.0023(13)	-0.0043(14)	-0.001(3)
Si2	0.25733(19)	0.1249(4)	0.20948(16)	0.0155(9)	0.034(2)	0.0060(13)	0.0061(13)	-0.0011(17)	-0.0019(13)	0.000(2)
Si3	0.1518(2)	0.1765(2)	0.3346(2)	0.0188(11)	0.023(2)	0.0167(19)	0.016(2)	-0.0042(15)	-0.0017(16)	0.0033(16)
Si4	0.2257(2)	0.3761(3)	0.33566(16)	0.0162(9)	0.0308(18)	0.0096(15)	0.0083(16)	-0.001(2)	0.0002(12)	-0.0013(18)
Si5	0.6434(2)	0.0704(2)	0.1641(2)	0.0168(11)	0.024(2)	0.0146(18)	0.0116(19)	0.0015(15)	0.0011(15)	0.0015(16)
O1	0.3209(5)	0.3724(8)	-0.0906(5)	0.026(2)						
O2	0.1575(5)	0.3700(7)	0.1472(5)	0.024(2)						
O3	0.1874(5)	0.1228(7)	0.2640(5)	0.025(2)						
O4	0.2445(4)	0.2879(7)	0.0201(6)	0.015(3)						
O5	0.2532(4)	0.0383(8)	0.1541(6)	0.013(3)						
O6	0.0648(5)	0.1658(7)	0.3307(5)	0.033(2)						
O7	0.3521(4)	0.3793(7)	0.1275(4)	0.0206(19)						
O8	0.3295(5)	0.1240(7)	0.2613(4)	0.0233(19)						
O9	0.2745(5)	0.3783(7)	0.2613(5)	0.025(2)						
O10	0.5547(5)	0.0806(7)	0.1601(5)	0.034(3)						
O11	0.2494(4)	-0.0369(7)	0.0179(6)	0.016(3)						
O12	0.2604(5)	0.2135(8)	0.1534(6)	0.020(3)						
O13	0.1708(6)	0.2849(6)	0.3323(5)	0.029(2)						
O14	0.2717(5)	0.3746(7)	0.4112(5)	0.026(2)						
O15	0.1772(5)	0.3762(8)	-0.0930(5)	0.025(2)						
O16	0.0480(7)	1.0429(8)	0.1545(7)	0.062(4)						
O17	0.1672(5)	0.4632(6)	0.3355(5)	0.029(2)						
O18	-0.0796(7)	0.9273(9)	0.2290(7)	0.066(4)						
O19	-0.0940(6)	0.7925(7)	0.1114(6)	0.053(3)						
O20 [#]	0.0474(18)	0.812(2)	0.0137(18)	0.090(7)						
O20 [#]	0.0374(17)	0.874(2)	0.0080(17)	0.090(7)						
O21 [#]	0.0531(13)	0.7134(16)	0.1513(13)	0.051(5)						
O21 [#]	0.0463(13)	0.7258(16)	0.1929(13)	0.051(5)						
O22	0.1504(5)	0.1248(7)	0.0458(4)	0.0226(19)						
O23	0.3452(5)	0.1270(7)	0.0257(4)	0.0226(19)						
O24 [#]	0.075(2)	1.022(2)	-0.0745(17)	0.086(7)						
O24 [#]	0.054(2)	1.016(2)	-0.0446(17)	0.086(7)						
O25 [#]	0.470(2)	0.002(3)	0.056(2)	0.147(11)						

O25 [#]	0.486(2)	-0.110(3)	0.160(2)	0.147(11)
O26 [#]	0.458(4)	-0.206(4)	0.051(3)	0.064(11)
O26 [#]	0.451(4)	-0.181(4)	0.018(3)	0.064(11)

Occ. – site occupancy; # atomic site is 50% occupied; U_{eq} is defined as a third of the trace of the orthogonalized U^j tensor

TABLE 4. Selected interatomic distances (in Å) for the structure of haiweeite.

U1		U2		Ca	
U1–O22	1.796(9)	U2–O2	1.776(9)	Ca–O7 ⁱⁱ	2.442(8)
U1–O23	1.786(9)	U2–O7	1.805(7)	Ca–O16	2.445(12)
U1–O4	2.324(10)	U2–O4	2.470(11)	Ca–O18	2.465(13)
U1–O5	2.481(11)	U2–O5 ⁱⁱ	2.336(11)	Ca–O18 ⁱⁱⁱ	2.731(13)
U1–O11	2.333(10)	U2–O9	2.230(9)	Ca–O19	2.386(11)
U1–O12	2.482(11)	U2–O11 ⁱⁱ	2.497(11)	Ca–O20	2.49(4)
U1–O14 ⁱ	2.237(9)	U2–O12	2.325(11)	Ca–O20'	2.39(4)
<U1–O _{U_r} >	1.791	<U2–O _{U_r} >	1.791	Ca–O21	2.45(3)
<U1–O _{Eq} >	2.37	<U2–O _{Eq} >	2.37	Ca–O21'	2.43(3)
				Ca–O24 ^{iv}	2.48(2)
				Ca–O24 ^{iv}	2.60(3)
				<Ca–O>	2.48
Si1		Si2		Si3	
Si1–O1	1.647(10)	Si2–O3	1.610(10)	Si3–O1 ^v	1.591(10)
Si1–O4	1.615(11)	Si2–O5	1.584(12)	Si3–O3	1.615(10)
Si1–O11 ⁱⁱ	1.586(11)	Si2–O8	1.615(9)	Si3–O6	1.601(10)
Si1–O15	1.638(10)	Si2–O12	1.614(12)	Si3–O13	1.582(9)
<Si1–O>	1.62	<Si2–O>	1.61	<Si2–O>	1.60
Si4		Si5			
Si4–O9	1.605(10)	Si5–O8 ^{vii}	1.617(9)		
Si4–O13	1.643(10)	Si5–O10	1.631(10)		
Si4–O14	1.594(10)	Si5–O15 ^{viii}	1.607(10)		
Si4–O17	1.638(10)	Si5–O17 ^{ix}	1.587(9)		
<Si4–O>	1.62	<Si5–O>	1.61		
O1–O3 ⁱ	2.611(13)	O7–O20 ^{vi}	2.88(4)	O18–O24 ^{iv}	2.87(4)
O1–O4	2.709(14)	O7–O20 ^{vi}	2.95(4)	O19–O24 ^{iv}	2.75(3)
O1–O6 ⁱ	2.581(13)	O7–O21 ^{vi}	2.97(3)	O19–O26 ^{xiv}	2.93(6)
O1–O11 ⁱⁱ	2.665(14)	O8–O10 ^{vii}	2.618(13)	O20–O20'	0.91(4)
O1–O13 ⁱ	2.635(14)	O8–O12	2.638(13)	O20–O21	2.82(4)
O1–O15	2.631(13)	O8–O15 ^v	2.614(11)	O20–O26 ^{xiv}	2.54(6)
O1–O24 ^{vi}	2.87(3)	O8–O17 ^{vi}	2.648(13)	O20–O26 ^{xiv}	2.65(6)
O2–O5 ⁱⁱ	2.902(14)	O8–O21 ^{vi}	2.97(2)	O20'–O24	2.65(4)
O2–O9	2.963(13)	O9–O13	2.643(13)	O20'–O24 ^{iv}	2.78(5)
O2–O12	2.919(14)	O9–O14	2.687(13)	O20'–O24'	2.24(4)
O2–O25 ⁱⁱ	2.65(4)	O9–O17	2.662(13)	O20'–O24 ^{iv}	2.37(5)
O2–O26 ⁱⁱ	2.93(6)	O9–O18 ^{ix}	2.765(16)	O20'–O26 ^{xiv}	2.99(6)
O3–O5	2.603(14)	O10–O15 ^{viii}	2.617(13)	O21–O21'	0.79(3)
O3–O6	2.615(13)	O10–O17 ^{ix}	2.653(13)	O21'–O21 ⁱⁱⁱ	2.65(3)
O3–O8	2.601(13)	O10–O21 ^{vi}	2.73(3)	O22–O24 ^{xv}	2.94(4)
O3–O12	2.716(14)	O10–O21 ^{vi}	2.83(3)	O22–O24 ^{xv}	2.86(4)
O3–O13	2.629(13)	O10–O25	2.67(4)	O23–O25	2.95(4)
O4–O11 ⁱⁱ	2.496(14)	O11–O15 ^{vi}	2.699(14)	O24–O24'	0.65(5)
O4–O12	2.629(15)	O11–O22	2.970(13)	O24'–O24 ^{iv}	2.59(5)
O4–O15	2.684(14)	O11–O23	2.921(13)	O25–O25 ^{xvi}	2.29(5)
O4–O22	2.925(13)	O13–O14	2.653(13)	O25–O25'	2.48(6)
O4–O23	2.941(13)	O13–O17	2.539(12)	O25–O26	2.97(7)
O5–O8	2.670(13)	O14–O17	2.662(13)	O25–O26'	2.71(7)
O5–O11	2.666(15)	O14–O19 ^{ix}	2.751(14)	O25'–O26	2.40(7)
O5–O12	2.497(16)	O14–O22 ^v	2.799(12)	O25'–O26'	2.78(7)
O5–O22	2.970(13)	O14–O23 ^v	2.964(12)	O26–O26'	0.70(8)
O6–O13	2.575(13)	O15–O17 ^{xi}	2.627(14)		

O6–O16 ^x	2.720(15)	O15–O19 ^{xii}	2.862(15)
O7–O9	2.787(12)	O16–O18 ⁱⁱⁱ	2.720(18)
O7–O11 ⁱⁱ	2.955(12)	O16–O22 ^{xiii}	2.946(15)
O7–O12	2.933(14)	O16–O24 ^{iv}	2.83(4)
O7–O16 ^{vi}	3.000(15)	O16–O24 ^{iv}	2.83(4)
O7–O18 ^{ix}	2.940(15)	O18–O19	2.862(16)

Symmetry codes: (i) $-x+1/2, -y+1/2, z-1/2$; (ii) $-x+1/2, y+1/2, z$; (iii) $-x, y, -z+1/2$;
(iv) $-x, -y+2, -z$; (v) $-x+1/2, -y+1/2, z+1/2$; (vi) $-x+1/2, y-1/2, z$; (vii) $-x+1, y, -z+1/2$;
(viii) $x+1/2, -y+1/2, -z$; (ix) $x+1/2, y-1/2, -z+1/2$; (x) $-x, y-1, -z+1/2$; (xi) $x, -y+1, z-1/2$;
(xii) $-x, -y+1, -z$; (xiii) $x, y+1, z$; (xiv) $x-1/2, -y+1/2, -z$; (xv) $x, y-1, z$; (xvi) $-x+1, -y, -z$

TABLE 5 Bond-valence analysis for haiweeite.

	U1	U2	Ca	Si1	Si2	Si3	Si4	Si5	Σ BV	Assignment
O1				0.94		1.09			1.93	O
O2		1.70							1.70	O
O3					1.04	1.02			2.06	O
O4	0.59	0.45		1.02					2.06	O
O5	0.44	0.58			1.11				2.13	O
O6						1.06			1.06	OH
O7		1.61	0.28						1.89	O
O8					1.02			1.02	2.04	O
O9		0.71					1.05		1.76	O
O10								0.98	0.98	OH
O11	0.58	0.42		1.11					2.11	O
O12	0.44	0.59			1.03				2.06	O
O13						1.12	0.95		2.07	O
O14	0.70						1.08		1.78	O
O15				0.96				1.05	2.01	O
O16			0.27						0.27	H ₂ O
O17							0.96	1.11	2.07	O
O18			0.39						0.39	H ₂ O
O19			0.32						0.32	H ₂ O
O20			0.24↓×0.5						0.24	H ₂ O
O20'			0.32↓×0.5						0.32	H ₂ O
O21			0.27↓×0.5						0.27	H ₂ O
O21'			0.29↓×0.5						0.29	H ₂ O
O22	1.63								1.63	O
O23	1.67								1.67	O
O24			0.25↓×0.5						0.25	H ₂ O
O24'			0.18↓×0.5						0.18	H ₂ O
O25									0.00	H ₂ O
O25'									0.00	H ₂ O
O26									0.00	H ₂ O
O26'									0.00	H ₂ O
Σ BV	6.05	6.06	2.04	4.03	4.20	4.29	4.04	4.16		

Notes: Values are expressed in valence units (vu). Occupancy of the split O atoms implemented into calculations. Ca–O, bond strengths from

Brown and Altermatt (1985); Si–O bond strengths from Brese and O'Keeffe (1991); U⁶⁺–O bond strengths ($r_0 = 2.051$, $b = 0.519$) from Burns et al. (1997).

TABLE 6 Values of the bond-valence distribution factor *D* and the number of predicted and observed H₂O for uranyl silicate minerals based on the bond-valence approach.

Mineral (reference)	Formula	<i>D</i>	Predicted			Observed Total H ₂ O
			Total H ₂ O	Trans H ₂ O	Other H ₂ O	
Soddyite (Demartin et al. 1992)	[(UO ₂) ₂ SiO ₄](H ₂ O) ₂	0		-4		2
Kasolite (Fejfarová et al. 2011)	[(UO ₂)(SiO ₄) ^[2+6] Pb](H ₂ O)	0.75	1	-1		1
Boltwoodite (Burns 1998)	^[7] K[(UO ₂)SiO ₃ OH](H ₂ O)	0.75	1	-1		1
Natroboltwoodite (Burns 1998)	^[6] Na[(UO ₂)SiO ₃ OH](H ₂ O)	0.86	2	0	2	1
Weeksite (Fejfarová et al. 2012)	^[7] K ^[8] K[(UO ₂) ₂ Si ₅ O ₁₃](H ₂ O) ₄	1.13	3	1	2	4
Uranophane (Ginderów 1988)	^[7] Ca[(UO ₂)SiO ₃ OH] ₂ (H ₂ O) ₅	1.33	4	2	2	5
Cuprosklodowskite (Rosenzweig and Ryan 1975)	^[6] Cu ²⁺ [(UO ₂)SiO ₃ OH] ₂ (H ₂ O) ₆	1.50	5	2	3	6
Sklodowskite (Ryan and Rosenzweig 1977)	^[6] Mg[(UO ₂)(SiO ₃ OH)] ₂ (H ₂ O) ₆	1.50	5	2	3	6
Oursinite (Kubatko and Burns 2006)	^[6] (Co _{0.8} Mg _{0.2})[(UO ₂)(SiO ₃ OH)] ₂ (H ₂ O) ₆	1.50	5	2	3	6
Haiweeite (struct., this study)	^[8] Ca[(UO ₂) ₂ Si ₅ O ₁₂ (OH) ₂](H ₂ O) _n	1.80	6	3	3	6.28/7.50*
Haiweeite (calc., this study)	^[7] Ca[(UO ₂) ₂ Si ₅ O ₁₂ (OH) ₂](H ₂ O) _n	2.00	8	4	4	-
Haiweeite (Burns 2001)	^[6] Ca[(UO ₂) ₂ Si ₅ O ₁₂ (OH) ₂](H ₂ O) ₃	2.25	9	5	4	3

*Thermal analysis/structure refinement