

Structure refinements of coquimbite and paracoquimbite from the Hongshan Cu–Au deposit, NW China

ZHUMING YANG^{1,2} and GERALD GIESTER^{3,*}

¹ Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, PR China

² Institutions of Earth Sciences, Chinese Academy of Sciences, Beijing, PR China

³ Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr.14, 1090 Wien, Austria

*Corresponding author, e-mail: gerald.giester@univie.ac.at

Abstract: The crystal structures of coquimbite and paracoquimbite from the Hongshan Cu–Au deposit, NW China, were refined by single-crystal X-ray diffraction, including the positions of all non-H atoms and hydrogen atoms.

The unit-cell parameters of coquimbite are $a = 10.9644(15)$, $c = 17.090(3)$ Å, and $V = 1769.6(5)$ Å³, $Z = 4$ with space group $P\bar{3}1c$. The crystal structure was refined based on 1352 unique reflections to $R1(F) = 0.0301$, yielding the formula $\text{Fe}_{1.64}\text{Al}_{0.36}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. Among the three cation positions of coquimbite, the isolated octahedral one is dominantly occupied by Al, *i.e.* $\text{Al}_{0.660(3)}\text{Fe}_{0.340(3)}$. Consequently, the average Al–O interatomic distance is 1.9155 Å, smaller than the Fe–O distances, 2.002 Å for Fe(1), and 1.989 Å for Fe(2). Based on the structure data available for coquimbite in the literature, the ideal formula should be expressed as $\text{AlFe}_3(\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$ ($Z = 2$) or $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $x \sim 0.5$ rather than $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The simplified formula for coquimbite from Hongshan is $(\text{Al}_{0.66}\text{Fe}_{0.34})\text{Fe}_3(\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$.

The unit-cell parameters of paracoquimbite are $a = 10.9631(16)$, $c = 51.473(10)$ Å, and $V = 5357.7(15)$ Å³, $Z = 12$ with space group $R\bar{3}$. The crystal structure was refined using 2733 unique reflections to $R1(F) = 0.0550$, which led to the formula $\text{Fe}_{1.91}\text{Al}_{0.09}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. There are five non-equivalent octahedrally coordinated metal sites for Fe in the structure of paracoquimbite. The range of Fe^[6]–O interatomic distances in paracoquimbite (1.966 Å–2.016 Å) can well be compared with those found in various sulfate minerals of ferric iron.

Both minerals are characterized by a complex system of hydrogen bonds involving three types of H₂O molecules, respectively: those of $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ clusters, of isolated $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ octahedra and further interstitial (H₂O) groups. The interstitial H₂O molecules resemble a cyclohexane-like chair and are held in the structure solely by hydrogen bonding. In coquimbite H₂O_{W(2)} is disordered with two alternative orientations (H2B1 and H2B2), in paracoquimbite interstitial H₂O consists of two H₂O molecules, H₂O_{W(3)} and H₂O_{W(4)}. The range of the O–H stretching frequencies between ~ 2750 and ~ 3650 cm^{−1} from infrared spectroscopy for paracoquimbite is in fair accordance with the calculated values between ~ 2874 and ~ 3600 cm^{−1} from both the $d(\text{O} \dots \text{O})$ lengths and the $d(\text{H} \dots \text{O})$ lengths.

Key-words: coquimbite; paracoquimbite; crystal-structure refinement; hydrogen bonding; formula revision; NW China.

1. Introduction

Coquimbite (Rose, 1833; Breithaupt, 1841) and paracoquimbite (Ungemach, 1933) are secondary minerals found in the oxidized parts of iron sulfide deposits in arid regions. Paracoquimbite was considered as a “dimorph” or “polytype” with coquimbite (Robinson & Fang, 1971; Fang & Robinson, 1974; Majzlan *et al.*, 2010). The ideal chemical formulae for both minerals are commonly expressed as $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Palache *et al.*, 1951; Ramdohr & Strunz, 1978; Strunz & Nickel, 2001). Coquimbite and paracoquimbite with postulated ideal chemical formulae were identified by powder X-ray diffraction (PXRD) in the alteration products from experiments of controlled alteration of pyrite and marcasite (Sejkora *et al.*, 2015). But most samples of

coquimbite reported in the literature show essential substitution of Al for Fe. Considering the frequent replacement of Al for Fe, the general formula for coquimbite type minerals might be rewritten as $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ as proposed by Fang & Robinson (1970). It is often close to the composition $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, with $x \sim 0.5$.

The crystal structure of coquimbite was solved by Fang & Robinson (1970) and Giacobazzo *et al.* (1970), based on single-crystal X-ray data, later studied by synchrotron powder X-ray diffraction (Majzlan *et al.*, 2006). The hydrogen bonding scheme in coquimbite was first described by Demartin *et al.* (2010a) and Majzlan *et al.* (2010) revealing that the positions of hydrogen atoms correspond with the model reported for the isotopic synthetic compound $\text{Fe}^{3+}_2(\text{SeO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Giester & Miletich, 1995).

Table 1. Crystal data, data-collection information and refinement details for coquimbite and paracoquimbite.

	Coquimbite	Paracoquimbite
Formula	Fe _{1.64} Al _{0.36} (SO ₄) ₃ ·9H ₂ O	Fe _{1.91} Al _{0.09} (SO ₄) ₃ ·9H ₂ O
Formula weight	551.20	560.17
Space group	<i>P</i> 3̄1 <i>c</i>	<i>R</i> 3̄
<i>a</i> (Å)	10.9344(15)	10.9631(16)
<i>c</i> (Å)	17.090(3)	51.473(10)
<i>V</i> (Å ³), <i>Z</i>	1769.6(5), 4	5357.7(15), 12
<i>μ</i> (mm ^{−1})	1.819	2.029
Crystal dimensions (mm ³)	0.26 × 0.13 × 0.13	0.21 × 0.15 × 0.13
<i>F</i> (000), <i>ρ</i> _{calc} (g·cm ^{−3})	1125, 2.069	3422, 2.083
θ range for collection	3.73–27.46°	3.50–27.45°
Number of frames	660	938
Scan time (s/°)	8	5
<i>h, k, l</i> ranges	−14 → 14, −13 → 14, −22 → 21	−14 → 14, −14 → 13, −66 → 66
Total reflections measured	12100	18392
Unique reflections	1352 [<i>R</i> (int) = 2.91%]	2733 [<i>R</i> (int) = 5.13%]
Reflections used	1351 with <i>I</i> > 2σ(<i>I</i>)	2696 with <i>I</i> > 2σ(<i>I</i>)
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> 1(<i>F</i>), <i>wR</i> 2(<i>F</i> ²)[<i>I</i> > 2σ(<i>I</i>)]	3.01%, 6.10%	5.50%, 9.79%
No. of refined parameters	109	205
GoF on <i>F</i> ²	1.356	1.351
Δ <i>ρ</i> _{min} , Δ <i>ρ</i> _{max} (e/Å ³)	−0.33, 0.28	−0.40, 0.69

Rigaku Four-circle diffractometer equipped with a Saturn 724+ CCD detector, Mo tube ($\lambda K\alpha = 0.71073 \text{ \AA}$), graphite monochromator, ϕ -scans for distinct ω -angles, $\Delta\phi = 0.5^\circ/\text{frame}$, frame size: binned mode, $34 \mu\text{m}/2048 \times 2048$ pixels, detector-to sample distance: 45 mm. $T(K) = 293(2)$. Unit-cell parameters were obtained by least-squares refinements of 2θ values.

In the structure of coquimbite there are three non-equivalent metal sites, all with octahedral coordination. The increasing replacement of iron with aluminum is selective and may lead to a slightly different structure-type, such as the new mineral species aluminocoquimbite $\text{AlFe}^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Demartin *et al.*, 2010a and b). It was suggested that, if the Al/(Fe + Al) ratio exceeds ~ 0.25 (i.e., $x > \sim 0.5$ in $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), this new structure type is favored (Demartin *et al.*, 2010a, b; Majzlan *et al.*, 2010).

The sample of coquimbite from the Hongshan Cu–Au deposit, eastern Tianshan (NW China) was reported to have an ideal chemical formula $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Qin *et al.*, 2008). However, this composition had not been checked by single-crystal work (Majzlan *et al.*, 2010).

The crystal structure of paracoquimbite was solved by Robinson & Fang (1971) from single-crystal X-ray data and later refined based on a synchrotron powder X-ray diffraction study by Ackermann *et al.* (2009), but without hydrogen atom sites.

In the present study we used samples of coquimbite and paracoquimbite, both from the Hongshan Cu–Au deposit, eastern Tianshan (NW China) to conduct structure refinements with special focus on the substitutions of Al for Fe in both minerals and on the location of hydrogen sites in paracoquimbite. The general formula for coquimbite is further discussed for revision.

2. Sample description and experimental details

The Hongshan Cu–Au deposit is located in the southern margin of the Tu-Ha Basin in eastern Xinjiang, China. The deposit occurs in Mesozoic volcanic rocks, which consist of

quartz porphyry, rhyolitic porphyry and granitic porphyry. The ore minerals include chalcopryrite, pyrite, bornite, chalcocite, sphalerite and native gold (Xu *et al.*, 2008).

The Hongshan Cu–Au deposit is sited on the edge of the desert, which is one of the arid regions in eastern Xinjiang, where the temperature may reach 60°C , and the average annual precipitation is only 34.1 mm. The oxidation zone of the deposit is well developed with a thickness varying from 50 to 60 m. The secondary Fe-bearing sulfates are the dominant minerals in the oxidation zone. The associated minerals include coquimbite, paracoquimbite, parabutlerite, jarosite, ferricopiapite, rhomboclase, metasideronatriite, krausite, yavapaiite, voltaite, ferrinatriite, roemerite, and sideronatriite (Xu *et al.*, 2008).

The samples of coquimbite and paracoquimbite were obtained from the collection of the Museum of the Institute of Geology and Geophysics, Chinese Academy of Sciences, and originally described by Qin *et al.* (2008). The chemical compositions determined by wet chemical analysis had been reported by Qin *et al.* (2008) as (in wt%): SO_3 42.31, Fe_2O_3 28.61, Al_2O_3 0.01, MgO 0.01, H_2O 28.98, total 99.92 for coquimbite, and SO_3 42.55, Fe_2O_3 28.19, H_2O 28.72, CaO 0.02, MgO 0.01, Al_2O_3 0.03, Na_2O 0.02, total 99.54 for paracoquimbite. On the basis of 21 O atoms the empirical formula for coquimbite and paracoquimbite can be expressed as: $\text{Fe}_{2.02}\text{S}_{2.97}\text{H}_{18.1}\text{O}_{21}$ and $\text{Fe}_{1.99}\text{S}_{3.00}\text{H}_{18.00}\text{O}_{21}$, respectively, both close to the ideal values for $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. However, the chemical compositions by electron microprobe analyses show that Al_2O_3 varies from 0.01 wt% up to over 1.0 wt% (Qin *et al.*, 2008). Moreover, it is difficult to distinguish coquimbite from paracoquimbite since both minerals have similar chemical composition and are closely associated with each other.

Table 2. Atomic coordinates and isotropic atomic displacement parameters (in Å²) with estimated standard deviations (e.s.d.'s) in parentheses for coquimbite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Al	0	0	0.0	0.0148(3)
Fe(1)	0.3333	0.6667	0.25	0.01180(18)
Fe(2)	0.6667	0.3333	0.00252(3)	0.01692(15)
S	0.24478(5)	0.41509(5)	0.12311(3)	0.01538(13)
O(1)	0.31837(17)	0.34508(17)	0.09143(10)	0.0247(4)
O(2)	0.10834(17)	0.31138(17)	0.15505(10)	0.0230(4)
O(3)	0.22010(17)	0.49412(17)	0.06001(9)	0.0224(4)
O(4)	0.33577(16)	0.51624(16)	0.18439(9)	0.0182(3)
O _w (1)	0.16739(19)	0.07062(19)	0.06237(11)	0.0246(4)
H(1A)	0.218(3)	0.157(4)	0.0727(18)	0.037
H(1B)	0.180(3)	0.024(4)	0.0917(19)	0.037
O _w (2)	0.4490(2)	0.1162(2)	0.21010(12)	0.0325(4)
H(2A)	0.374(4)	0.043(4)	0.206(2)	0.049
H(2B1)	0.510(7)	0.106(7)	0.238(5)	0.049
H(2B2)	0.437(6)	0.179(7)	0.234(4)	0.049
O _w (3)	0.5721(2)	0.1623(2)	0.07126(11)	0.0306(4)
H(3A)	0.594(4)	0.104(4)	0.071(2)	0.046
H(3B)	0.533(4)	0.158(4)	0.116(2)	0.046

Occupancy: Al = 0.660(3)Al + 0.340(3)Fe; Fe(1) = 0.969(3)Fe + 0.031(3)Al; Fe(2) = 0.966(3)Fe + 0.034(3)Al; H(2B1) = 0.473(4)H; H(2B2) = 0.527(4)H.

Table 3. Anisotropic displacement parameters (in Å²) with estimated standard deviations (e.s.d.'s) in parentheses for coquimbite.

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Al	0.0127(4)	0.0127(4)	0.0191(6)	0	0	0.00634(18)
Fe(1)	0.0111(2)	0.0111(2)	0.0133(3)	0	0	0.00554(12)
Fe(2)	0.0178(2)	0.0178(2)	0.0151(3)	0	0	0.00892(10)
S	0.0152(3)	0.0127(2)	0.0174(3)	−0.00202(19)	−0.00064(19)	0.0063(2)
O(1)	0.0218(8)	0.0194(8)	0.0337(9)	−0.0089(7)	−0.0002(7)	0.0110(7)
O(2)	0.0192(8)	0.0186(8)	0.0251(8)	0.0005(7)	0.0032(7)	0.0050(7)
O(3)	0.0228(8)	0.0201(8)	0.0213(8)	0.0012(6)	−0.0043(6)	0.0084(7)
O(4)	0.0191(8)	0.0167(8)	0.0198(7)	−0.0054(6)	−0.0043(6)	0.0097(6)
O _w (1)	0.0250(9)	0.0161(8)	0.0316(9)	−0.0017(7)	−0.0088(7)	0.0094(7)
O _w (2)	0.0314(11)	0.0270(10)	0.0333(10)	−0.0024(8)	0.0022(8)	0.0102(8)
O _w (3)	0.0412(11)	0.0287(10)	0.0282(9)	0.0113(8)	0.0151(8)	0.0221(9)

Single-crystal X-ray data were collected using monochromatic MoK α -radiation on a Rigaku RA-Micro7HF diffractometer with a Saturn 724+ CCD detector. Data reduction, including intensity integration, correction for Lorentz and polarization effects, and absorption correction, was done using the software CrystalClear (Rigaku). The non-hydrogen atomic positions in coquimbite and in paracoquimbite from the references (Fang & Robinson, 1970; Robinson & Fang, 1971), respectively, were used as the start atomic parameters; positions of hydrogen atoms in coquimbite were taken in accordance to the isotypic selenate compound Fe₂(SeO₄)₃·9H₂O (Giestler & Miletich, 1995). The crystal structures for both minerals were refined with full-matrix least-squares techniques on *F*² using SHELX-97 (Sheldrick, 1997). The Fe:Al ratios at all octahedral *M* sites in both minerals were refined, assuming full occupancy at each site. The respective formula for coquimbite is Fe_{1.64}Al_{0.36}(SO₄)₃·9H₂O, and for paracoquimbite Fe_{1.91}Al_{0.09}(SO₄)₃·9H₂O. The positions of the

H atoms of the H₂O groups in paracoquimbite were identified in difference Fourier maps and were included in the final refinement with isotropic atomic displacement parameters, for all other atoms anisotropic displacement parameters were used.

The crystal data, data-collection information and refinement details for coquimbite and paracoquimbite are listed in Table 1. The atomic coordinates, site occupancy factors, displacement parameters, the relevant bond lengths and angles, and the bond-valence sums are shown in Tables 2–5 for coquimbite, and in Tables 6–9 for paracoquimbite, respectively.

3. Structure description of coquimbite

The principal structure features for coquimbite from Hongshan agree well with those reported by Demartin *et al.* (2010b) for samples of *Vulc1* (Vulcano Island, Italy),

Table 4. Relevant bond lengths (Å) and angles (°) in coquimbite.

AlO ₆		Fe(1)O ₆		SO ₄	
Al-O _w (1) × 6	1.9155(18)	Fe(1)-O(4) × 6	2.0018(15)	S-O(2)	1.4553(17)
H(1A)-O _w (1)-H(1B)	111(3)	Fe(2)O ₆		S-O(1)	1.4638(17)
H(2A)-O _w (2)-H(2B1)	112(5)	Fe(2)-O(3) × 3	1.9744(17)	S-O(4)	1.4865(15)
H(2A)-O _w (2)-H(2B2)	110(5)	Fe(2)-O _w (3) × 3	2.0035(18)	S-O(3)	1.4885(17)
H(3A)-O _w (3)-H(3B)	107(3)	Mean	1.989	Mean	1.474
D-H...A	d(D...H)	d(H...A)	∠DHA	d(D...A)	
O _w (1)-H(1A)...O(1)	0.84(3)	1.809	175.76	2.650	
O _w (1)-H(1B)...O(2)#1	0.78(3)	1.921	173.14	2.693	
O _w (2)-H(2A)...O(2)#1	0.82(4)	1.973	158.14	2.747	
O _w (2)-H(2B1)...O _w (2)#2	0.87(6)	1.886	169.54	2.748	
O _w (2)-H(2B2)...O _w (2)#3	0.86(6)	1.881	168.49	2.733	
O _w (3)-H(3A)...O(1)#4	0.79(4)	1.885	168.61	2.661	
O _w (3)-H(3B)...O _w (2)	0.87(4)	1.793	169.55	2.649	

Symmetry code for equivalent positions: #1 = $-x + y, -x, z$; #2 = $-x + y + 1, y, -z + 1/2$; #3 = $x, x - y, -z + 1/2$; #4 = $-y + 1, x - y, z$.

Table 5. Bond valences for coquimbite from Hongshan Cu–Au deposit.

	O(1)	O(2)	O(3)	O(4)	O _w (1)	O _w (2)	O _w (3)	Σ
Al					0.542 × 6			3.25
Fe(1)				0.519 × 6				3.11
Fe(2)			0.559 × 3				0.516 × 3	3.23
S	1.542	1.578	1.442	1.450				6.01
H(1A)		0.230			0.770			1.00
H(1B)	0.254				0.746			1.00
H(2A)		0.205				0.795		1.00
H(2B1)						0.376, 0.097		0.47
H(2B2)						0.416, 0.111		0.53
H(3A)	0.248						0.752	1.00
H(3B)						0.255	0.745	1.00
Σ	2.04	2.01	2.00	1.97	2.06	2.05	2.01	

The bond valences were calculated from the curves of [Brese & O'Keeffe \(1991\)](#); hydrogen bond strengths were calculated from the curves of [Ferraris & Ivaldi \(1988\)](#).

Utah (Dexter No.7 mine, San Rafael Swell, Utah) and Chile (La Alcaparosa, Chile). There are three non-equivalent octahedrally coordinated metal sites. Aluminium is the dominant cation at the Al position, whereas iron is dominant at the other two sites. The structure of coquimbite is based on [Fe₃(SO₄)₆(H₂O)₆]^{3−} clusters, isolated [Al(H₂O)₆]³⁺ octahedra, and interstitial (H₂O) groups shown in [Fig. 1](#). The cluster with composition [Fe₃(SO₄)₆(H₂O)₆]^{3−} is formed by one Fe(1)- and two Fe(2)-centered octahedra and six SO₄ tetrahedra, which share only corners. Each [Fe₃(SO₄)₆(H₂O)₆]^{3−} cluster interacts through hydrogen bonds of interstitial six H₂O molecules with its neighboring clusters, forming a chain along [001]. These chains, in turn, are linked via hydrogen bonds with the isolated [Al(H₂O)₆]³⁺ octahedra.

The [Al(H₂O)₆]³⁺ octahedron in coquimbite from Hongshan is nearly regular. The average Al–O_w interatomic distance, 1.9155 Å, is only slightly larger than those reported for the samples of *Vulc1*, *Utah* and *Chile* (1.8796 Å, 1.8808 Å, and 1.9048 Å, respectively; [Demartin et al., 2010b](#)), and the sample of *Utah USA* (1.896 Å, [Majzlan et al., 2010](#)). These mean values of Al^{VI}–O interatomic distances in coquimbite can also be well

compared with those found in the synthetic compounds Al₂(SO₄)₃·5H₂O (1.8755–1.8861 Å, [Fischer et al., 1996a](#)), Al₂(SO₄)₃·8H₂O (1.8781–1.8813 Å, [Fischer et al., 1996b](#)), Al₂(SO₄)₃·10.5H₂O (1.8803–1.8842 Å, [Fischer et al., 1996c](#)), and in alunogen Al₂(SO₄)₃·16H₂O (1.885–1.890 Å, [Fang & Robinson, 1976](#); 1.879–1.881 Å, [Sun et al., 2015](#)).

The ⟨Al–O_w⟩ interatomic distance in coquimbite is smaller than the ⟨Fe–O⟩ distances known for ferric iron in six-coordination. Respective values are 2.0018 Å for Fe(1)–O and 1.989 Å for Fe(2)–O (in detail: Fe(2)–O 1.9744 Å, and Fe(2)–O_w 2.0035 Å). Similar Fe–O bond lengths can be seen in the samples of *Vulc1*, *Utah* and *Chile*, i.e. (Fe(2)–O: 2.0029 Å, 2.0018 Å, 2.0008 Å; Fe(3)–O: 1.9710 Å, 1.9747 Å, 1.9763 Å; Fe(3)–O_w: 1.9950 Å, 1.9982 Å, 2.0038 Å, [Demartin et al., 2010b](#)), and *Utah USA* (Fe(2)–O: 2.002 Å; Fe(3)–O: 1.976 Å; Fe(3)–O_w: 2.003 Å, [Majzlan et al., 2010](#)). In aluminocoquimbite the differences between Al–O and Fe–O distances are much the same. The Al(3)–O_w bond lengths are 1.8920 Å and 1.8702 Å, while the Fe(1)–O distance is 1.9867 Å, that of Fe(2)–O is 2.0012 Å ([Demartin et al., 2010b](#)).

Table 6. Atomic coordinates and isotropic atomic displacement parameters (in Å²) with estimated standard deviations (e.s.d.'s) in parentheses for paracoquimbite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Fe(1)	0	0	0	0.0168(3)
Fe(2)	0	0	0.5	0.0200(3)
Fe(3)	0	0	0.250778(17)	0.0132(2)
Fe(4)	0	0	0.167717(18)	0.0164(2)
Fe(5)	0	0	0.665242(18)	0.0183(2)
S(1)	0.24958(9)	0.41606(9)	0.875549(18)	0.0160(2)
S(2)	0.58362(9)	0.75489(9)	0.959461(18)	0.0169(2)
O(1)	0.3257(3)	0.3492(3)	0.86496(6)	0.0238(6)
O(2)	0.6547(3)	0.6824(3)	0.96979(6)	0.0265(6)
O(3)	0.1144(3)	0.3109(3)	0.88629(5)	0.0234(6)
O(4)	0.6854(3)	0.8913(3)	0.94873(5)	0.0252(6)
O(5)	0.2224(3)	0.4933(3)	0.85463(5)	0.0210(6)
O(6)	0.5056(3)	0.7783(3)	0.98065(5)	0.0242(6)
O(7)	0.3399(3)	0.5187(3)	0.89583(5)	0.0201(6)
O(8)	0.4823(3)	0.6631(3)	0.93932(5)	0.0197(6)
O _w (1)	0.1719(3)	0.0732(3)	0.85513(6)	0.0289(7)
H(1A)	0.180(6)	0.025(6)	0.8643(10)	0.043
H(1B)	0.213(6)	0.158(6)	0.8576(10)	0.043
O _w (2)	0.9277(3)	0.8273(3)	0.97877(6)	0.0283(7)
H(2A)	0.846(6)	0.774(6)	0.9755(10)	0.042
H(2B)	0.975(6)	0.812(6)	0.9708(11)	0.042
O _w (3)	0.4481(4)	0.1164(4)	0.90124(8)	0.0369(8)
H(3A)	0.379(7)	0.039(7)	0.9012(12)	0.055
H(3B)	0.442(7)	0.161(7)	0.9070(13)	0.055
O _w (4)	0.8843(4)	0.5480(4)	0.92896(7)	0.0352(8)
H(4A)	0.958(7)	0.619(7)	0.9279(12)	0.053
H(4B)	0.850(7)	0.566(7)	0.9227(13)	0.053
O _w (5)	0.5954(3)	0.4345(4)	0.85517(7)	0.0310(7)
H(5A)	0.627(6)	0.470(6)	0.8691(11)	0.047
H(5B)	0.525(6)	0.408(6)	0.8544(11)	0.047
O _w (6)	0.5741(4)	0.4109(3)	0.97561(7)	0.0323(7)
H(6A)	0.592(6)	0.494(6)	0.9759(11)	0.048
H(6B)	0.538(6)	0.384(6)	0.9633(11)	0.048

Occupancy: Fe(1) = 0.921(4)Fe + 0.080(4)Al; Fe(2) = 0.980(4)Fe + 0.020(4)Al; Fe(3) = 0.974(4)Fe + 0.026(4)Al; Fe(4) = 0.980(4)Fe + 0.020(4)Al; Fe(5) = 0.971(4)Fe + 0.029(4)Al.

Table 7. Anisotropic displacement parameters (in Å²) with estimated standard deviations (e.s.d.'s) in parentheses for paracoquimbite.

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Fe(1)	0.0150(4)	0.0150(4)	0.0204(7)	0	0	0.0075(2)
Fe(2)	0.0177(4)	0.0177(4)	0.0246(7)	0	0	0.0088(2)
Fe(3)	0.0125(3)	0.0125(3)	0.0147(4)	0	0	0.00625(14)
Fe(4)	0.0165(3)	0.0165(3)	0.0161(5)	0	0	0.00825(15)
Fe(5)	0.0191(3)	0.0191(3)	0.0166(5)	0	0	0.00954(16)
S(1)	0.0156(4)	0.0133(4)	0.0186(4)	−0.0014(3)	−0.0007(3)	0.0070(3)
S(2)	0.0133(4)	0.0164(4)	0.0195(4)	−0.0002(3)	−0.0019(3)	0.0064(3)
O(1)	0.0206(13)	0.0220(14)	0.0300(16)	−0.0077(12)	−0.0002(11)	0.0115(11)
O(2)	0.0202(14)	0.0249(15)	0.0367(17)	−0.0016(12)	−0.0091(12)	0.0130(12)
O(3)	0.0201(13)	0.0192(13)	0.0256(14)	0.0005(11)	0.0027(11)	0.0060(11)
O(4)	0.0223(14)	0.0207(14)	0.0260(15)	0.0024(12)	−0.0005(12)	0.0057(12)
O(5)	0.0226(14)	0.0166(13)	0.0200(14)	0.0025(11)	−0.0026(11)	0.0070(11)
O(6)	0.0216(14)	0.0234(14)	0.0226(14)	−0.0041(11)	0.0021(11)	0.0076(12)
O(7)	0.0223(13)	0.0181(13)	0.0214(14)	−0.0059(11)	−0.0050(11)	0.0114(11)
O(8)	0.0182(13)	0.0231(14)	0.0202(13)	−0.0036(11)	−0.0049(10)	0.0120(11)
O _w (1)	0.0340(17)	0.0189(14)	0.0341(18)	−0.0005(13)	−0.0149(14)	0.0133(13)
O _w (2)	0.0173(14)	0.0265(15)	0.0386(18)	−0.0130(13)	−0.0033(13)	0.0091(12)
O _w (3)	0.0351(18)	0.0261(18)	0.041(2)	−0.0075(15)	0.0031(15)	0.0092(15)
O _w (4)	0.0284(18)	0.0369(19)	0.035(2)	0.0060(15)	−0.0018(15)	0.0125(15)
O _w (5)	0.0247(15)	0.0344(18)	0.0365(18)	−0.0103(14)	−0.0013(14)	0.0166(15)
O _w (6)	0.0425(19)	0.0276(16)	0.0309(17)	−0.0042(14)	−0.0163(14)	0.0206(15)

Table 8. Relevant bond lengths (Å) and angles (°) in paracoquimbite.

Fe(1)O ₆		Fe(3)O ₆		S(1)O ₄	
Fe(1)-O _w (2) × 6	1.977(3)	Fe(3)-O(8) × 3	2.000(3)	S(1)-O(3)	1.457(3)
Fe(2)O ₆		Fe(3)-O(7) × 3	1.997(3)	S(1)-O(1)	1.464(3)
Fe(2)-O _w (5) × 6	1.992(3)	Mean	1.999	S(1)-O(5)	1.489(3)
		Fe(4)O ₆		S(1)-O(7)	1.491(3)
H(1A)-O _w (1)-H(1B)	121(6)	Fe(4)-O(5) × 3	1.966(3)	Mean	1.475
H(2A)-O _w (2)-H(2B)	112(6)	Fe(4)-O _w (1) × 3	2.016(3)	S(2)O ₄	
H(3A)-O _w (3)-H(3B)	116(8)	Mean	1.991	S(2)-O(4)	1.455(3)
H(4A)-O _w (4)-H(4B)	98(8)	Fe(5)O ₆		S(2)-O(2)	1.463(3)
H(5A)-O _w (5)-H(5B)	113(6)	Fe(5)-O(6) × 3	1.974(3)	S(2)-O(8)	1.485(3)
H(6A)-O _w (6)-H(6B)	104(6)	Fe(5)-O _w (6) × 3	2.003(3)	S(2)-O(6)	1.485(3)
		Mean	1.989	Mean	1.472
D-H...A	d(D-H)	d(H...A)	∠DHA	d(D...A)	
O _w (1)-H(1A)...O(3)#1	0.75(6)	1.979	175.23	2.726	
O _w (1)-H(1B)...O(1)	0.81(6)	1.868	172.80	2.674	
O _w (2)-H(2A)...O(2)	0.81(6)	1.839	168.98	2.634	
O _w (2)-H(2B)...O(4)#2	0.75(6)	1.938	173.1	2.680	
O _w (3)-H(3A)...O(3)#1	0.80(7)	2.016	153.96	2.762	
O _w (3)-H(3B)...O _w (4)#3	0.61(7)	2.183	172.06	2.783	
O _w (4)-H(4A)...O(4)#2	0.80(7)	2.095	144.26	2.780	
O _w (4)-H(4B)...O _w (3)#4	0.60(6)	2.213	159.91	2.783	
O _w (5)-H(5A)...O _w (3)#4	0.81(6)	1.827	169.11	2.625	
O _w (5)-H(5B)...O(1)	0.68(6)	2.017	160.08	2.666	
O _w (6)-H(6A)...O(2)	0.84(6)	1.845	166.55	2.664	
O _w (6)-H(6B)...O _w (4)#3	0.73(6)	1.947	173.18	2.670	

Symmetry code for equivalent positions: #1 = -x + y, -x, z; #2 = -y + 2, x - y + 1, z; #3 = -x + y + 1, -x + 1, z; #4 = -y + 1, x - y, z.

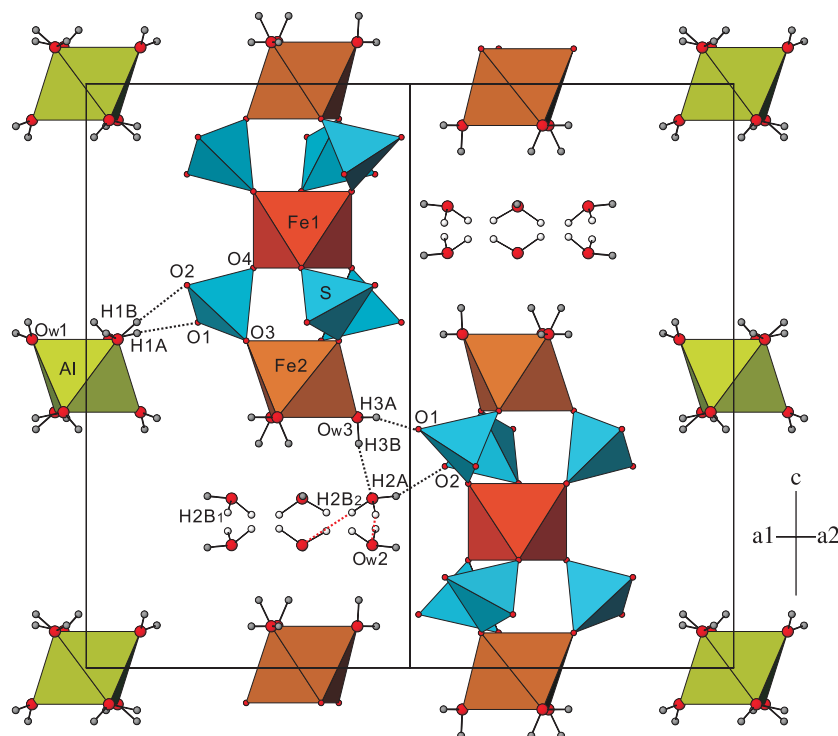
Table 9. Bond valences for paracoquimbite from Hongshan Cu–Au deposit.

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O _w (1)	O _w (2)	O _w (3)	O _w (4)	O _w (5)	O _w (6)	Σ
Fe(1)										0.555 × 6					3.33
Fe(2)													0.533 × 6		3.20
Fe(3)							0.526 × 3	0.521 × 3							3.14
Fe(4)					0.572 × 3				0.499 × 3						3.21
Fe(5)						0.559 × 3								0.517 × 3	3.23
S(1)	1.541		1.570		1.440		1.433								5.97
S(2)		1.545		1.579		1.456		1.456							6.02
H(1A)			0.214						0.786						1.00
H(1B)	0.240								0.760						1.00
H(2A)		0.264								0.736					1.00
H(2B)				0.237						0.763					1.00
H(3A)			0.198								0.802				1.00
H(3B)											0.810	0.190			1.00
H(4A)				0.191								0.809			1.00
H(4B)											0.190	0.810			1.00
H(5A)											0.270		0.730		1.00
H(5B)	0.245												0.755		1.00
H(6A)		0.246												0.754	1.00
H(6B)												0.243		0.757	1.00
Σ	2.03	2.06	1.98	2.01	2.01	2.02	1.96	1.98	2.05	2.05	2.07	2.05	2.02	2.03	

The bond valences were calculated from the curves of [Brese & O'Keeffe \(1991\)](#); hydrogen bond strengths were calculated from the curves of [Ferraris & Ivaldi \(1988\)](#).

The coquimbite-type selenate Fe³⁺₂(SeO₄)₃·9H₂O ([Giester & Miletich, 1995](#)), a compound synthesized in the absence of aluminum, shows no relevant differences of mean Fe–O distances, which for all three cation positions are within the narrow spread of 1.992–1.9935 Å.

The range of Fe^[6]–O interatomic distances in coquimbite and mean values can be well compared with those found in minerals of the system Fe³⁺–S–O–H (e.g. lausenite Fe³⁺₂(SO₄)₃·5H₂O: ⟨1.979⟩, ⟨1.985⟩ Å, [Majzlan et al., 2006](#); kornelite Fe³⁺₂(SO₄)₃·~7.75H₂O: ⟨1.983⟩, ⟨1.987⟩ Å, [Ackermann et al., 2009](#); quenstedtite



$\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 11\text{H}_2\text{O}$: $\langle 1.993 \rangle$, $\langle 1.996 \rangle$ Å, [Thomas *et al.*, 1974](#)) and some sulfate minerals of ferric iron recently studied by our group ([Yang *et al.*, 2015](#); [Yang & Giester, 2016, 2018](#)).

In the structure of coquimbite there are three types of H₂O molecules: [Fe₃(SO₄)₆(H₂O)₆]³⁻ clusters with O_W(3)...O distances of 2.65–2.66 Å; isolated [Al(H₂O)₆]³⁺ octahedra with O_W(1)...O distances 2.65–2.69 Å; and interstitial (H₂O) groups with O_W(2)...O distances 2.73–2.75 Å (Table 4). The interstitial H₂O molecules resemble a cyclohexane-like chair, which are held in the structure solely by hydrogen bonding, as described by Demartin *et al.* (2010b). This interstitial H₂O_W(2) molecule is disordered with two alternative orientations in which one of the two hydrogen atoms keeps the same position (H2A), whereas the other one (H2B) statistically occupies two separate positions (H2B1 and H2B2), each with an occupancy of ~0.5. This feature corresponds to that observed for the coquimbite samples of *Vulc1*, *Utah* and *Chile* (Demartin *et al.*, 2010b) and in the isotopic compound Fe₂(SeO₄)₃·9H₂O (Giester & Miletich, 1995) with two types of hydrogen-bonded network variants and locally reduced symmetry.

A comparison of the site occupancies for coquimbite and aluminocoquimbite is given in [Table 10](#). The x -value in $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ for coquimbite actually is reported within the range from 0.32 to 0.63. In the structures of both minerals there are three non-equivalent octahedrally coordinated metal sites for Al and Fe. For aluminocoquimbite Al occupies the $M(3)$ site, the ideal formula can be expressed as $\text{FeAl}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ or $\text{AlFe}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ([Demartin *et al.*, 2010a](#) and [b](#)). For coquimbite, since Al usually occupies the $M(1)$ site, the extended ideal formula can be expressed as $\text{AlFe}_3(\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$ ($Z=2$) or, following the 50% rule, as $(\text{Al,Fe})\text{Fe}_3(\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$, where the $M(1)$ site usually is not fully occupied by Al, but with $\text{Al} > 0.5$. In order to separate possible end-members, this description is more useful than the formula $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, because the value of x varies only from 0.25 to 0.5 even if the $M(1)$ site is occupied by 0.5Al to 1.0Al. The simplified formula for coquimbite from Hongshan is $(\text{Al}_{0.66}\text{Fe}_{0.34})\text{Fe}_3(\text{SO}_4)_6 \cdot 18\text{H}_2\text{O}$.

Since coquimbite has a distinctly different chemical composition as compared to paracoquimbite, both minerals should not be considered as polytypes. Furthermore, they may have different conditions of formation. The presence of aluminum ions in the aqueous solution might favor the formation of coquimbite, while in its absence, paracoquimbite may be preferred (Demartin *et al.*, 2010b).

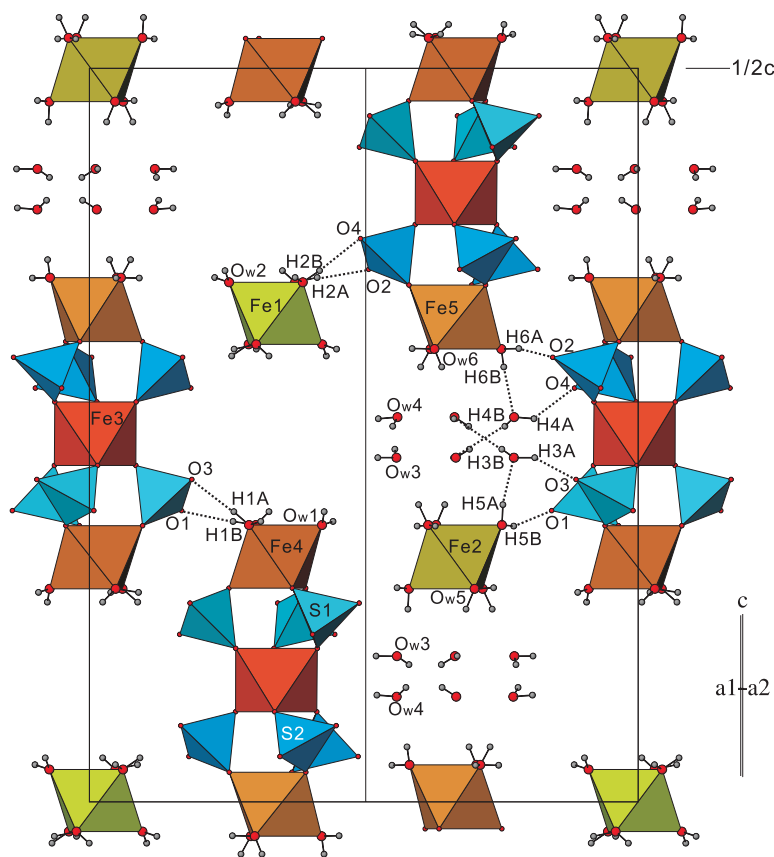


Fig. 2. The crystal structure of paracoquimbite viewed from $[1\ 1\ 0]$. Small red circle = O; large red circle = O_w , gray circle = H.

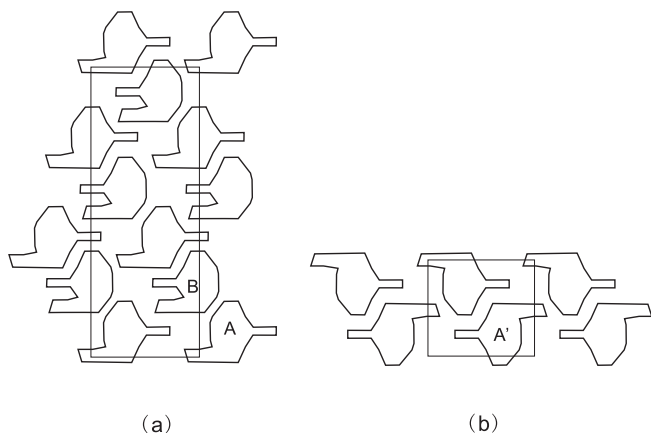


Fig. 3. Comparison of the crystal structures for paracoquimbite (a) and coquimbite (b) in blocks both viewed from $[1\ 1\ 0]$.

5. Structural features and hydrogen bonding in paracoquimbite

The structure details of paracoquimbite from Hongshan are just the same as described by Robinson & Fang (1971) for samples from Chuquicamata, Chile. There are five non-equivalent octahedrally coordinated metal sites. The atomic arrangement of paracoquimbite is also based on

$[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ clusters, isolated $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ octahedra, and six interstitial (H_2O) groups as shown in Fig. 2. The cluster with composition $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ is formed by each one Fe(4)-, Fe(5)-, and Fe(3)-centered octahedron as well as by six SO_4 tetrahedra, which share only corners. Fe(1) and Fe(2) form two isolated $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ octahedra. The $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ clusters are oriented with their long axis parallel to $[00\ 1]$ and are part of a linear chain with the sequence: –isolated $[\text{Fe}(1)(\text{H}_2\text{O})_6]^{3+}$ octahedra – $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ cluster – six (H_2O) groups – isolated $[\text{Fe}(1)(\text{H}_2\text{O})_6]^{3+}$ octahedra – six (H_2O) groups – $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ cluster –. These chains, in turn, interact via hydrogen bonds with a $1/2c$ shift along $[00\ 1]$ to form the structure of paracoquimbite.

The coquimbite and paracoquimbite structures can be compared on the basis of blocks. In each structure individual layers are made up of blocks, and an individual block is made up of a $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ cluster, an isolated octahedron and six (H_2O) groups. There are three types of blocks: A, B and A', as seen in Fig. 3. In block A, the isolated $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ octahedron and six (H_2O) groups are separated on two sides of the $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$ cluster. In block B, the isolated $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ octahedron and six (H_2O) groups are sited on the same side of the polyhedral cluster. In block A', the isolated $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ octahedron and six (H_2O) groups are separated on two sides of the $[\text{Fe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_6]^{3-}$

Table 10. Comparison of the site occupancies for coquimbite and aluminocoquimbite.

Locality	x^a	$M1(2b)^b$	$M2(2c)^b$	$M3(4f)^b$	Reference
Dexter no 7 mine (Utah USA) ^c	0.32	Al _{0.64} Fe _{0.36}	Fe	Fe	Giacovazzo <i>et al.</i> (1970)
Dexter no 7 mine (Utah USA) ^c	0.50	Al	Fe	Fe	Demartin <i>et al.</i> (2010b)
Dexter no 7 mine (Utah USA) ^c	0.56	Al	Fe _{0.97} Al _{0.03}	Fe _{0.96} Al _{0.04}	Majzlan <i>et al.</i> (2010)
Hongshan (China) ^c	0.36	Al _{0.66} Fe _{0.34}	Fe _{0.97} Al _{0.03}	Fe _{0.97} Al _{0.03}	This work
Iron Mountain (California USA) ^c	0.53	Al _{0.91} Fe _{0.09}	Fe	Fe _{0.93} Al _{0.07}	Majzlan <i>et al.</i> (2006)
Javier Ortega (Peru) ^c	0.63				Frost <i>et al.</i> (2014)
La Alcaparrosa (Chile) ^c	0.38	Al _{0.76} Fe _{0.24}	Fe	Fe	Demartin <i>et al.</i> (2010b)
Tierra Amarilla (Chile) ^c	0.45	Al _{0.90} Fe _{0.10}	Fe	Fe	Fang & Robinson (1970)
Vulcano (Sicily Italy) ^c	0.50	Al	Fe	Fe	Demartin <i>et al.</i> (2010b)
Vulcano (Sicily Italy) ^d	1.00	Fe	Fe	Al	Demartin <i>et al.</i> (2010a and b)

^a x based on $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$;^b (Wyckoff position);^c coquimbite;^d aluminocoquimbite.

cluster. The paracoquimbite structure is made up of block A and B, while the coquimbite structure is only made up of block A'. The coquimbite and paracoquimbite structures differ not only in the manner in which individual blocks are stacked along the [001] direction, but also in the compositions of blocks. This further shows that paracoquimbite should not be considered as a "dimorph" or "polytype" with coquimbite.

The range of Fe–O interatomic distances (1.966 Å–2.016 Å) and mean S–O distances in paracoquimbite (1.472 Å–1.475 Å) is similar to those found in the coquimbite and aluminocoquimbite samples.

The system of hydrogen-bonds in paracoquimbite is shown in detail in Fig. 2. There are again three types of H_2O molecules belonging to 1) clusters with $\text{O}_w(1) \dots \text{O}$ (2.67–2.73 Å) and $\text{O}_w(6) \dots \text{O}$ (2.66–2.67 Å); 2) the isolated octahedra with $\text{O}_w(2) \dots \text{O}$ (2.63–2.68 Å) and $\text{O}_w(5) \dots \text{O}$ (2.63–2.67 Å); and 3) the interstitial (H_2O) groups with $\text{O}_w(3) \dots \text{O}$ (2.76–2.78 Å) and $\text{O}_w(4) \dots \text{O}$ (~2.78 Å). The interstitial six H_2O molecules are arranged in a way similar to that observed for coquimbite (Fig. 1), but without disorder.

The FTIR spectrum of paracoquimbite shows a characteristic absorption with a maximum at $\sim 3397 \text{ cm}^{-1}$ (Qin *et al.*, 2008). It suggests there exists strong O–H bonding in paracoquimbite. There is a sharp absorption corresponding to the OH bending at $\sim 1634 \text{ cm}^{-1}$, which indicates that the hydrous component in paracoquimbite actually is molecular H_2O . The range of the O–H stretching frequencies between ~ 2750 and $\sim 3650 \text{ cm}^{-1}$ from infrared spectroscopy is approximately in accordance with values in the range ~ 2874 to 3600 cm^{-1} calculated from both the $d(\text{O} \dots \text{O})$ lengths and the $d(\text{H} \dots \text{O})$ lengths by using the equations suggested by Libowitzky (1999).

Acknowledgements: The authors acknowledge the help of Dr. HaoXiang and Liang Tongling with the single-crystal structure measurement. The project was supported by the National Natural Science Foundation of China (No. 41272063).

References

- Ackermann, S., Lazic, B., Armbruster, T., Doyle, S. (2009): Thermodynamic and crystallographic properties of kornelite $[\text{Fe}_2(\text{SO}_4)_3 \cdot \sim 7.75\text{H}_2\text{O}]$ and paracoquimbite $[\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}]$. *Am. Mineral.*, **94**, 1620–1628.
- Breithaupt, A. (1841): Coquimbites ferricus kürzer Coquimbit. in "Vollständiges Handbuch der Mineralogie, Volume 2", **100**. Arnoldische Buchhandlung Dresden und, Leipzig.
- Brese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192–197.
- Demartin, F., Castellano, C., Gramaccioli, C.M., Campostrini, I. (2010a): Aluminum-for-iron substitution, hydrogen bonding and a novel structural type in coquimbite-like minerals. *Can. Mineral.*, **48**, 323–333.
- , —, —, — (2010b): Aluminocoquimbite, $\text{AlFe}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, a new aluminium iron sulphate from Grotta Dell'Allume, Vulcano, Aeolian Islands, Italy. *Can. Mineral.*, **48**, 1465–1468.
- Dowty, E. (2016): Atoms V6.5.0 for atomic structure display. Shape Software, 521 Hidden 14 Valley Road, Kingsport, TN 37663 USA.
- Fang, J.H. & Robinson, P.D. (1970): Crystal structures and mineral chemistry of hydrated ferric sulfates. I. The crystal structure of coquimbite. *Am. Mineral.*, **55**, 1534–1540.
- , — (1974): Polytypism in coquimbite and paracoquimbite. *Neues Jahrb. Mineral. Monatsh.*, **1974**, 89–91.
- , — (1976): Alunogen, $\text{Al}_2(\text{H}_2\text{O})_{12}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$: Its atomic arrangement and water content. *Am. Mineral.*, **61**, 311–317.
- Ferraris, G. & Ivaldi, G. (1988): Bond valence vs. bond length in $\text{O} \dots \text{O}$ hydrogen bonds. *Acta Cryst.*, **B44**, 341–344.
- Fischer, T., Eisenmann, B., Kniep, R. (1996a): Crystal structure of dialuminum tris(sulfate) pentahydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$. *Z. Kristallogr.*, **211**, 471–472.
- , —, — (1996b): Crystal structure of dialuminum tris(sulfate) octahydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. *Z. Kristallogr.*, **211**, 473–474.
- , —, — (1996c): Crystal structure of dialuminum tris(sulfate) 10.5-hydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot 10.5\text{H}_2\text{O}$. *Z. Kristallogr.*, **211**, 475–476.
- Frost, R.L., Gobac, Ž.Ž., López, A., Xi, Y., Scholz, R., Lana, C., Lima, R.M.F. (2014): Characterization of the sulphate mineral coquimbite, a secondary iron sulphate from Javier Ortega mine, Lucanas Province, Peru – Using infrared, Raman spectroscopy and thermogravimetry. *J. Mol. Struct.*, **1063**, 251–258.

- Giacovazzo, C., Menchetti, S., Scordari, F. (1970): The crystal structure of coquimbite. *Atti. Accad. Naz. Lin.*, Serie 8, **49**, 129–140.
- Giester, G. & Miletich, R. (1995): Crystal structure and thermal decomposition of the coquimbite-type compound $\text{Fe}_2(\text{SeO}_4)_3 \cdot 9\text{H}_2\text{O}$. *Neues Jahrb. Mineral. Monatsh.*, **1995**, 211–223.
- Hawthorne, F.C., Krivovichev, S.V., Burns, P.C. (2000): The crystal chemistry of sulfate minerals. in “Sulfate minerals: crystallography, geochemistry, and environmental significance”, C.N. Alpers, J.L. Jambor, B.K. Nordstrom, eds., *Rev. Mineral. Geochem.*, **40**, 1–112.
- Libowitzky, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatsh. Chem.*, **130**, 1047–1059.
- Majzlan, J., Navrotsky, A., McCleskey, B., Alpers, C.N. (2006): Thermodynamic properties and crystal structure refinement of ferricopiapite, coquimbite, rhomboclase, and $\text{Fe}_3(\text{SO}_4)_2(\text{H}_2\text{O})_5$. *Eur. J. Mineral.*, **18**, 175–186.
- Majzlan, J., Djordjević, T., Kolitsch, U., Schefer, J. (2010): Hydrogen bonding in coquimbite, nominally $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and the relationship between coquimbite and paracoquimbite. *Mineral. Petrol.*, **100**, 241–248.
- Palache, C., Berman, H., Frondel, C. (1951): The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana, Yale University 1837–1892, Volume II. John Wiley and Sons Inc., New York, 7th edition, revised and enlarged, **1124**, 532–534.
- Qin, K.Z., Ding, K.S., Xu, Y.X., Miao, Y., Fang, T.H., Xu, X.W. (2008): Tremendous crystal of paracoquimbite and its polytype coquimbite found for the first time in Hongshan Hs-epithermal Cu–Au deposit, eastern Tianshan, NW-China, and its significance. *Acta Petrol. Sin.*, **24**, 1112–1122 (in Chinese with English abstract).
- Ramdohr, P. & Strunz, H. (1978): Klockmanns Lehrbuch der Mineralogie. 16. Aufl., Ferdinand Enke Verlag, Stuttgart, **876**, 608 p.
- Robinson, P.D. & Fang, J.H. (1971): Crystal structures and mineral chemistry of hydrated ferric sulphates: II. The crystal structure of paracoquimbite. *Am. Mineral.*, **56**, 1567–1572.
- Rose, H. (1833): Ueber einige in Südamerika vorkommende Eisenoxydsalze. *Annalen der Physik und Chemie*, **27**, 309–319.
- Sejkora, J., Malikova, R., Novak, M. (2015): Alteration products from experiments of controlled alteration of pyrite and marcasite. *Bull. Mineral.-petrol. Odd. Nar. Muz. (Praha)* **23**, 261–270.
- Sheldrick, G.M. (1997): SHELXL-97, Program for the refinement of crystal structures. University of Göttingen, Germany.
- Strunz, H. & Nickel E.H. (2001): Strunz Mineralogical Tables. Chemical-structural Mineral Classification System. 9. Auflage, E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller), Stuttgart, **870**, 385 p.
- Sun, X.X., Sun, Y.Z., Yu, J.G. (2015): Crystal structure of aluminum sulfate hexadecahydrate and its morphology. *Cryst. Res. Technol.*, **50**, 293–298.
- Thomas, J.N., Robinson, P.D., Fang, J.H. (1974): Crystal structures and mineral chemistry of hydrated ferric sulfates. IV. The crystal structure of quenstedtite. *Am. Mineral.*, **59**, 582–586.
- Ungemach, M.H. (1933): Sur quelques minéraux nouveaux. *Comptes Rendus de L'Académie des Sciences Paris*, **197**, 1132–1134.
- Xu, Y.X., Qin, K.Z., Ding, K.S., Li, J.X., Miao, Y., Fang, T.H., Xu, X.W., Li, D.M., Luo, X.Q. (2008): Geochronology evidence of Mesozoic metallogenesis and Cenozoic oxidation at Hongshan HS-epithermal Cu–Au deposit, Kalatage region, Eastern Tianshan, and its tectonic and paleoclimatic significances. *Acta Petrol. Sin.*, **24**, 2371–2383 (in Chinese with English abstract).
- Yang, Z.M. & Giester, G. (2016): Hydrogen-bonding system in amarillite, $\text{NaFe}(\text{SO}_4)_2(\text{H}_2\text{O})_6$: the structure refinement. *Eur. J. Mineral.*, **28**, 953–958.
- , — (2018): Hydrogen bonding in goldichite, $\text{KFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$: structure refinement. *Mineral. Petrol.*, in press.
- Yang, Z.M., Giester, G., Ding, K.S., Li, H. (2015): Crystal structure of sideronatrite-2M, $\text{Na}_2\text{Fe}(\text{SO}_4)_2(\text{OH})(\text{H}_2\text{O})_3$, a new polytype from Xitieshan lead-zinc deposit, Qinghai Province, China. *Eur. J. Mineral.*, **27**, 427–432.

Received 4 October 2017

Modified version received 22 November 2017

Accepted 30 November 2017