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THE CRYSTAL STRUCTURE OF COBALTARTHURITE FROM THE BOU AZZER DISTRICT, MOROCCO: THE LOCATION OF HYDROGEN ATOMS IN THE ARTHURITE STRUCTURE-TYPE

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ABSTRACT

The crystal structure of cobaltarthurite, ideally $Co^{2+}Fe^{3+}_2(AsO_4)_2(OH)_2•4H_2O$, monoclinic, $P2_1/c$, a 10.2635(9), b 9.7028(8), c 5.5711(5) Å, β 94.2070(10)°, from Khder, Bou Azzer district, Morocco, has been refined to R_1 = 1.8%, wR_2 = 6.4% using 1343 unique [$F_o > 4\sigma(F_o)$] reflections collected with a Bruker 1K SMART Platform CCD diffractometer and Mo$K\alpha$ radiation. This is the best determination of the structure of an arthurite-group mineral yet obtained, and for the first time has allowed the determination of hydrogen positions. The hydrogen bonding scheme proposed in previous studies on arthurite-group minerals is confirmed with one change.

Keywords: cobaltarthurite, arthurite group, crystal structure, hydrogen bonding, Bou Azzer, Morocco.

SOMMAIRE

La structure cristalline de la cobaltarthurite, dont la composition idéale est $Co^{2+}Fe^{3+}_2(AsO_4)_2(OH)_2•4H_2O$, monoclinique, $P2_1/c$, a 10.2635(9), b 9.7028(8), c 5.5711(5) Å, β 94.2070(10)°, provenant de Khder, district de Bou Azzer, au Maroc, a été affinée jusqu'à un résidu R_1 de 1.8% (wR_2 = 6.4%) en utilisant 1343 réflexions uniques [$F_o > 4\sigma(F_o)$] prélevées avec un diffractomètre Bruker 1K SMART à platteforme CCD et un rayonnement Mo$K\alpha$. Ces résultats de précision élevée ont permis la meilleure détermination de la structure d'un minéral du groupe de l'arthurite jusqu'à ce point, et pour la première fois, ont mené à la détermination de la position des atomes d'hydrogène. Le schéma des liaisons hydrogène proposé antérieurement se trouve confirmé, avec un seul changement.

(Traduit par la Rédaction)

Mots-clés: cobaltarthurite, groupe de l'arthurite, structure cristalline, liaisons hydrogène, Bou Azzer, Maroc.

INTRODUCTION

Cobaltarthurite was first described by Jambor *et al.* (2002) from near Mazarrón, Murcia, Spain, where it occurs as globular to pellet-like aggregates of yellowish, radial fibers and dark brown non-fibrous microscopic intergrowths. A Rietveld refinement (R_{wp} = 0.077) by Raudsepp & Pani (2002) confirmed the mineral to be isostructural with other members of the arthurite group: whitmoreite, $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2•4H_2O$, earlshannonite, $Mn^{2+}Fe^{3+}_2(PO_4)_2(OH)_2•4H_2O$, ojuelaite, $Zn^{2+}Fe^{3+}_2(AsO_4)_2(OH)_2•4H_2O$, and arthurite, $Cu^{2+}Fe^{3+}_2(AsO_4)_2(OH)_2•4H_2O$. Previously, structures had been determined for whitmoreite (Moore *et al.* 1974), arthurite (Keller & Hess (1978) and ojuelaite (Hughes *et al.* 1996). Hydrogen atom positions were not located in any of these structure determinations.

The discovery of distinct single crystals of cobaltarthurite at Khder in the Bou Azzer district, Morocco, by Georges Favreau prompted the current study. It was hoped that high-quality single-crystal data collected using a CCD detector would allow the location of hydrogen atoms and the confirmation or revision of the hydrogen bonding scheme proposed in the earlier studies.

CRYSTAL-STRUCTURE REFINEMENT

A subhedral fragment of cobaltarthurite was used for the collection of structure data. Structure-data collection was performed on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD detector. A full sphere of three-dimensional data was collected. Fifty duplicate frames acquired at the

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end of the data collection indicated that no significant decay had taken place. The measured intensities were corrected for Lorentz and polarization effects using the program SAINT, and an empirical absorption-correction was applied using the program SADABS (Bruker 1997). The SHELXL97 software (Sheldrick 1997) was used for the determination and refinement of the structure.

The positions of all non-hydrogen atoms were taken from the earlier determinations of the structures of arthurite-group minerals. Refinement of the structure with full occupancies assigned to the Co and Fe sites and with all displacement parameters considered to be isotropic yielded R_1 = 3.06%. With all displacement parameters refined as anisotropic, R_1 improved to 2.21%. Attempts were made to refine the site occupancies of the Co and Fe sites, including refining the Co site with joint occupancy by both Co and Fe. The best results were obtained by assigning only Co to the Co site. The site occupancies refined to 0.97 for the Co site and 0.98 for the Fe site, with R_1 improving to 2.14%.

Difference maps showed peaks that could unambiguously be assigned to all H atoms on the basis of bond-valence considerations and reasonable hydrogen-bond geometries. The refinement with all H atoms located at the sites provided by the difference synthesis improved the R_1 to 1.80%, with the Co and Fe site occupancies refining to 0.95 and 0.99, respectively. Although it was possible to refine the hydrogen positions, this tended to result in somewhat less reasonable distances and did not improve R_1.

Electron-microprobe analyses of crystals closely associated with that used in the structure analysis provided the data given in Table 1. Only Co, Fe, Ca and As were detected. Assuming all Fe to be 3+ and the Fe site to be fully occupied by Fe, the empirical formula is $(Co_{0.60}Fe_{0.16}Ca_{0.01})_{\Sigma 0.77}Fe_2(AsO_{3.85}OH_{0.15})_2(OH)_2 \bullet 4H_2O$, based upon 2.00 As atoms per formula unit. Clearly, the cation total (Co + Fe + Ca) provided by the EMP analyses (2.77 *apfu*) is significantly lower that that provided by the structure determination (2.93 *apfu*).

Table 2 gives the details of the data collection and structure refinement, Table 3, the final fractional coordinates and displacement parameters, Table 4, selected interatomic distances, Table 5, hydrogen bond distances and angles, and Table 6, the bond valences. A listing of the observed and calculated structure-factors can be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. CHEMICAL COMPOSITION OF COBALTARTHURITE

	wt.%*	atoms**
Co	6.4	0.60
Fe	21.9	2.16
Ca	0.2	0.01
As	27.1	2.00

* Average result of three electron-microprobe analyses
** Atoms in formula on the basis of 2 As *apfu*

DESCRIPTION OF THE STRUCTURE

The structure of cobaltarthurite, as with other members of the arthurite group, is based upon a unique corrugated sheet of Fe^{3+}–O octahedra. Each Fe^{3+}–O octahedron shares an O1–O1 edge and two OH vertices with equivalent edges and vertices of adjacent octahedra. Two remaining vertices (O2 and O4) are shared with AsO_4 tetrahedra. Three of the four tetrahedron vertices link to octahedron vertices in the same sheet of Fe^{3+}–O octahedra, whereas the remaining corner links to a Co^{2+}–O octahedron. Two *trans* vertices of the Co^{2+}–O octahedra link to AsO_4 tetrahedra attached to different sheets, thereby forming bridges between the sheets. The four remaining Co^{2+} ligands are H_2O molecules (OW1 and OW2). The corrugated sheet of Fe^{3+}–O octahedra decorated with AsO_4 tetrahedra is shown in Figure 1. The complete structure, including hydrogen bonds, is shown in Figure 2.

The hydrogen bonding scheme proposed by Moore *et al.* (1974) for whitmoreite and generally accepted by later investigators [Keller & Hess (1978) for arthurite, Hughes *et al.* (1996) for ojuelaite, Raudsepp & Pani (2002) for cobaltarthurite] is confirmed with one change. The hydrogen bonds are: OH–H…O2, OW1–H…O2, OW1–H…O3, OW2–H…O4, and OW2–H…OW1, the last of these being the only correction to the earlier-proposed scheme.

TABLE 2. DATA-COLLECTION AND STRUCTURE-REFINEMENT DETAILS FOR COBALTARTHURITE

Diffractometer	Bruker 1K SMART Platform CCD
X-ray radiation / power	Mo*K*α (λ 0.71073 Å) / 50 kV, 45 mA
Temperature	298(2) K
Crystal system, space group	monoclinic, $P2_1/c$
Unit-cell dimensions	*a* 10.2635(9) Å
	b 9.7028(8)Å
	c 5.5711(5)Å
	β 94.2070(10)°
Volume	553.30(8) $Å^3$
Absorption coefficient	10.08 mm^{-1}
F(000)	534
Crystal size	0.10 × 0.06 × 0.02 mm
θ range for data collection	1.99 to 28.29°
Index ranges	$-13 \leq h \leq 13, -12 \leq k \leq 12, -7 \leq l \leq 7$
Reflections collected / unique	4843 / 1343 [R_{int}* = 0.0225]
Completeness to θ = 28.29°	97.7%
Refinement method	Full-matrix least-squares on F^2
Parameters refined	92
GooF†	0.603
R indices [$F_o > 4\sigma(F_o)$]	R_1‡ = 1.80%, wR_2§ = 6.36%
R indices (all data)	R_1 = 2.36%, wR_2 = 7.12%
Largest diff. peak / hole	+0.48 / -0.46 $e/Å^3$

* $R_{int} = \Sigma \mid F_o^2 - F_o^2(\text{mean}) \mid / \Sigma [F_o^2]$
† $\text{GooF} = S = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$
‡ $R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$
§ $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$
$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$,
where *a* is 0, *b* is 12.994, and *P* is $[2F_c^2 + \text{Max}(F_o^2,0)] / 3$

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR COBALTARTHURITE

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Co	0	0	0	0.0100(3)	0.0118(3)	0.0106(3)	-0.0017(2)	0.0020(2)	-0.0023(2)	0.0107(2)
Fe	0.4561(1)	0.1363(1)	0.3397(1)	0.0091(2)	0.0075(2)	0.0059(2)	0.0003(1)	0.0008(1)	0.0000(1)	0.0075(2)
As	0.2973(1)	0.4277(1)	0.3278(1)	0.0074(2)	0.0087(2)	0.0062(2)	-0.0001(1)	0.0011(1)	0.0001(1)	0.0074(1)
O1	0.3989(2)	0.4848(2)	0.1178(3)	0.0116(9)	0.0113(9)	0.0067(8)	-0.0004(7)	0.0038(7)	-0.0032(7)	0.0097(4)
O2	0.3558(2)	0.4897(2)	0.5995(3)	0.0117(10)	0.0088(8)	0.0077(9)	-0.0013(7)	-0.0009(7)	0.0002(7)	0.0095(4)
O3	0.1483(2)	0.4904(2)	0.2594(3)	0.0086(10)	0.0187(10)	0.0136(10)	0.0030(8)	0.0016(7)	0.0034(7)	0.0136(4)
O4	0.2970(2)	0.2542(2)	0.3204(3)	0.0119(10)	0.0091(9)	0.0117(9)	-0.0013(7)	0.0010(7)	-0.0006(7)	0.0109(4)
OH	0.5417(2)	0.2328(2)	0.0783(3)	0.0120(9)	0.0116(9)	0.0099(9)	0.0021(7)	0.0040(7)	0.0030(7)	0.0110(4)
OW1	0.1289(2)	0.9062(2)	0.2936(4)	0.0190(12)	0.0258(11)	0.0164(11)	-0.0013(9)	0.0029(9)	-0.0021(9)	0.0203(5)
OW2	0.0460(2)	0.1903(2)	0.1361(4)	0.0206(12)	0.0189(11)	0.0334(13)	-0.0142(10)	0.0021(10)	-0.0028(9)	0.0243(5)
H	0.5816	0.1789	0.9815							0.05
H11	0.1991	0.9085	0.2478							0.05
H12	0.1252	0.9326	0.4318							0.05
H21	0.1096	0.2173	0.2328							0.05
H22	0.9839	0.2383	0.1819							0.05

TABLE 4. SELECTED BOND-DISTANCES (Å) IN COBALTARTHURITE

Co–OW2 (×2)	2.039(2)	Fe–OH	1.989(2)
Co–O3 (×2)	2.103(2)	Fe–O4	1.991(2)
Co–OW1 (×2)	2.222(2)	Fe–OH	1.995(2)
<Co–O>	2.138	Fe–O2	2.035(2)
		Fe–O1	2.063(2)
As–O3	1.665(2)	Fe–O1	2.093(2)
As–O4	1.684(2)	<Fe–O>	2.035
As–O2	1.697(2)		
As–O1	1.715(2)		
<As–O>	1.690		

TABLE 5. HYDROGEN BOND DISTANCES (Å) AND ANGLES (°) IN COBALTARTHURITE

	O–H	H…O	O-H…O	O–O
OH–H…O2	0.875	2.007	149.09	2.794(3)
OW1–H11…O2	0.782	2.107	152.76	2.825(3)
OW1–H12…O3	0.814	1.970	169.60	2.775(3)
OW2–H21…O4	0.856	1.981	153.07	2.772(3)
OW2–H22…OW1	0.844	2.009	156.84	2.805(3)

H11–OW1–H12: 114.07; H21–OW2–H22: 101.48

TABLE 6. BOND-VALENCE SUMMATIONS FOR COBALTARTHURITE

	O1	O2	O3	O4	OH	OW1	OW2	$\Sigma_c v$
Co			0.329 ×2→			0.239 ×2→	0.391 ×2→	1.919
Fe	0.440 0.405	0.474		0.534	0.537 0.528			2.919
As	1.151	1.208	1.317	1.251				4.932
H		0.19			0.81			1.000
H11		0.17				0.83		1.000
H12			0.22			0.78		1.000
H21				0.22			0.78	1.000
H22						0.18	0.82	1.000
$\Sigma_a v$	1.996	2.043	1.867	2.006	1.876	2.029	1.991	

Co–O, Fe–O and As–O bond strengths from Brese & O'Keeffe (1991); based upon full occupancy.
H-bond strengths from Ferraris & Ivaldi (1988), based on O…O distances. Valence summations are expressed in valence units.

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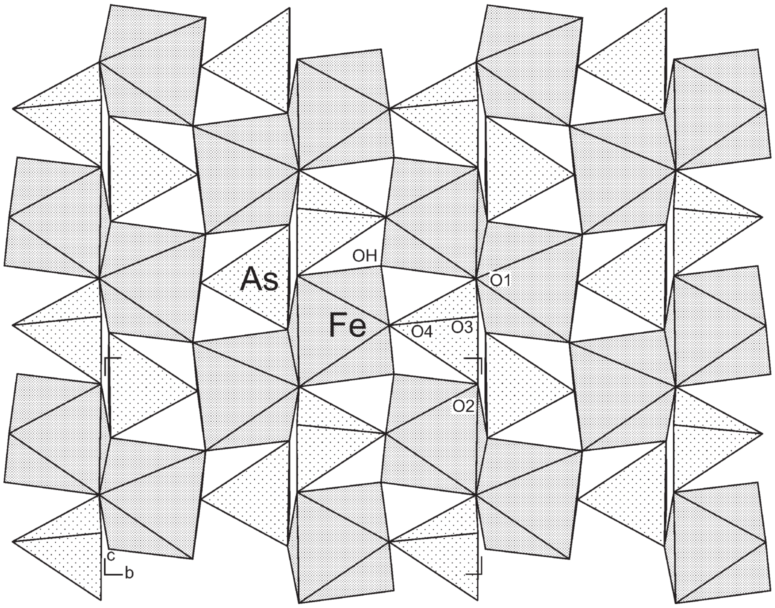

FIG. 1. Sheet of Fe^{3+}–O octahedra with AsO_4 tetrahedra in cobaltarthurite.

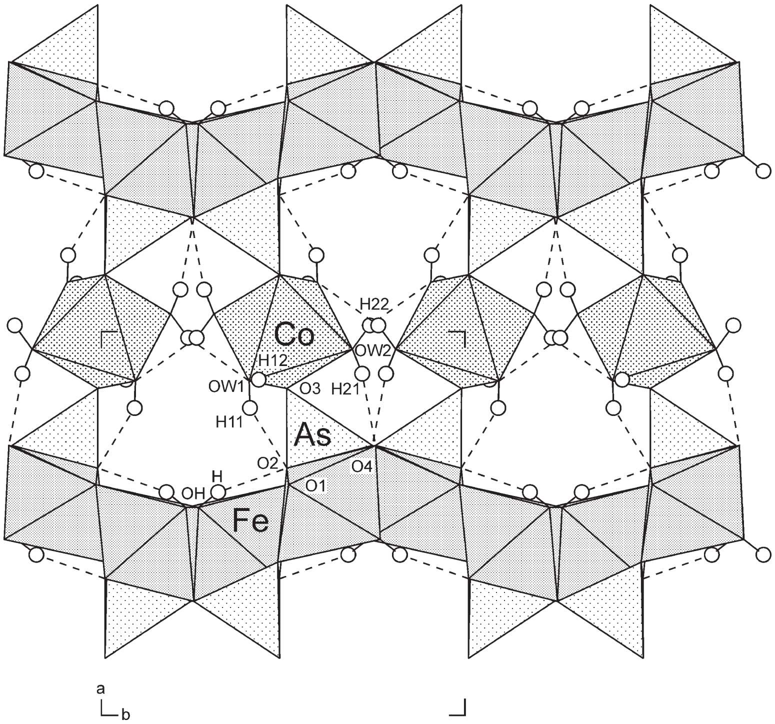

FIG. 2. Crystal structure of cobaltarthurite showing hydrogen bonds.

REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr*. **B47**, 192-197.

FERRARIS, G. & IVALDI, G. (1988): Bond valence *vs*. bond length in O…O hydrogen bonds. *Acta Crystallogr.* **B44**, 341-344.

HUGHES, J.M., BLOODAXE, E.S., KOBEL, K.D. & DREXLER, J.W. (1996): The atomic arrangement of ojuelaite, $ZnFe^{3+}{}_2(AsO_4)_2(OH)_2{\bullet}4H_2O$. *Mineral. Mag*. **60**, 519-521.

JAMBOR, J.L., VIÑALS, J., GROAT, L.A. & RAUDSEPP, M. (2002): Cobaltarthurite, $Co^{2+}Fe^{3+}{}_2(AsO_4)_2(OH)_2{\bullet}4H_2O$, a new member of the arthurite group. *Can. Mineral*. **40**, 725-732.

KELLER, P. & HESS, H. (1978): Die Kristallstruktur von Arthurit, $CuFe^{3+}{}_2[(H_2O)|(OH)_2|(AsO_4)_2]$. *Neues Jahrb. Mineral., Abh.* **133**, 291-302.

MOORE, P.B., KAMPF, A.R. & IRVING, A.J. (1974): Whitmoreite, $Fe^{2+}Fe^{3+}{}_2(OH)_2(H_2O)_4[PO_4]_2$, a new species: its description and atomic arrangement. *Am. Mineral*. **59**, 900-905.

RAUDSEPP, M. & PANI, E. (2002): The crystal structure of cobaltarthurite, $Co^{2+}Fe^{3+}{}_2(AsO_4)_2(OH)_2{\bullet}4H_2O$: a Rietveld refinement. *Can. Mineral*. **40**, 733-737.

SHELDRICK, G.M. (1997): *SHELXL97. Program for the Solution and Refinement of Crystal Structures*. University of Göttingen, Göttingen, Germany.

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