

THE CRYSTAL STRUCTURE OF COBALTARTHURITE, $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$: A RIETVELD REFINEMENT

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ABSTRACT

The crystal structure of cobaltarthurite from near Pastrana, southeastern Spain [monoclinic, a 10.2694(4), b 9.6790(3), c 5.5723(2) Å, β 94.277(2)°, $P2_1/c$], has been refined to R_{wp} and R_B indices of 7.7 and 1.7%, respectively, using the Rietveld method and X-ray powder-diffraction data. Cobaltarthurite is a newly discovered Co-dominant analogue of arsenate members of the arthurite group, with ideal formula $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Results of the Rietveld refinement confirm that cobaltarthurite is isostructural with other members of the group. Electron-probe micro-analyses show that the formula is of ideal stoichiometry, with minor substitution of Mg, Mn, Ni, Cu and Ca for Co, and trace P and S substitution for As.

Keywords: cobaltarthurite, arsenate, chemical analysis, arthurite group, crystal structure, Rietveld refinement, X-ray powder-diffraction.

SOMMAIRE

Nous avons affiné la structure cristalline de la cobaltarthurite découverte près de Pastrana, dans le sud-est de l'Espagne [monoclinique, a 10.2694(4), b 9.6790(3), c 5.5723(2) Å, β 94.277(2)°, $P2_1/c$] selon la méthode de Rietveld utilisée avec des données en diffraction X, jusqu'à des indices de concordance R_{wp} et R_B de 7.7 and 1.7%, respectivement. La cobaltarthurite est un nouveau membre du groupe de l'arthurite, un arséniate à dominance de cobalte, dont la formule idéale serait $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Les résultats de l'affinement confirment que la cobaltarthurite est isostructurale avec les autres membres du groupe. Les analyses à la microsonde électronique montrent que la formule possède la stoechiométrie idéale, avec une incorporation mineure de Mg, Mn, Ni, Cu et Ca pour le Co, et des traces de P et de S en substitution pour As.

(Traduit par la Rédaction)

Mots-clés: cobaltarthurite, arséniate, analyse chimique, groupe de l'arthurite, structure cristalline, affinement de Rietveld, diffraction X, méthode des poudres.

INTRODUCTION

Cobaltarthurite, of ideal formula $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, from near Pastrana, southeastern Spain, is a newly discovered member of the arthurite group (Jambor *et al.* 2002). Previously known members of the arthurite group have the general formula $A^{2+}\text{Fe}^{3+}_2(\text{XO}_4)_2(\text{O},\text{OH})_2 \cdot 4\text{H}_2\text{O}$, where $A^{2+} = \text{Cu}, \text{Fe}, \text{Mn}, \text{Zn}$; $X = \text{As}^{5+}, \text{P}^{5+}, \text{S}^{6+}$ (Mandarino 1999). In Table 1, we summarize compositional data for members of the arthurite group. Debye–Scherrer X-ray powder-diffraction data (Jambor *et al.* 2002) suggest that the structure of cobaltarthurite is similar to that of other members of the arthurite group, in particular to that of ojuelaite. Single-crystal structure refinements have been reported for all known members

of the group, except for earlshannonite (Table 1). Lacking crystals of cobaltarthurite sufficiently large for single-crystal structure refinement, we report here the results of a Rietveld refinement of the structure using X-ray powder-diffraction data, together with results of electron-probe micro-analyses that complement the data provided by Jambor *et al.* (2002).

EXPERIMENTAL METHODS

Electron-probe micro-analysis

Electron-probe micro-analyses of cobaltarthurite were done on a fully automated CAMECA SX-50 in-

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strument, operating in the wavelength-dispersion mode, with the following operating conditions: excitation voltage 20 kV, beam current 5 nA, peak count-time 20 s, background count-time 10 s, spot diameter 10 μm . At beam currents greater than 5 nA and at spot sizes less than 10 μm , cobaltarthurite was visibly damaged by the electron beam, and X-ray counts from all elements were not constant over time. Data reduction was done using the "PAP" $\phi(\rho Z)$ method (Pouchou & Pichoir 1985). For the elements considered, the following standards, X-ray lines and crystals were used: elemental Co, $\text{CoK}\alpha$, LIF; diopside, $\text{MgK}\alpha$, TAP; tennantite, $\text{CuK}\alpha$, LIF; diopside, $\text{CaK}\alpha$, PET; hematite, $\text{FeK}\alpha$, LIF; synthetic MnSiO_3 , $\text{MnK}\alpha$, LIF; synthetic Ni_2SiO_4 , $\text{NiK}\alpha$, LIF; tennantite, $\text{AsL}\alpha$, TAP; apatite, $\text{PK}\alpha$, PET; barite, $\text{SK}\alpha$, PET; hematite, $\text{OK}\alpha$, W/Si multilayer dispersion element. Results are presented in Table 2.

X-ray powder diffraction

Several grams of material were hand-picked under a binocular microscope from the full width of the cobaltarthurite veinlet described by Jambor *et al.* (2002). Although the crystals of cobaltarthurite measure only 2–3 μm in width, they are acicular and attain a length of up to 75 μm . To minimize preferred orientation in the powder mount, the sample was ground for 5 minutes under ethanol in a vibratory McCrone Micronising Mill (McCrone Scientific Ltd., London, U.K.). Samples were gently pressed from the bottom of an aluminum sample holder against a ground glass slide; the cavity in the holder is $43 \times 24 \times 1.5$ mm in size. The textured surface of the glass minimizes preferred orientation of anisotropic grains at the diffracting surface of the powder.

Step-scan X-ray powder-diffraction data were collected over the range $5\text{--}80^\circ 2\theta$ with $\text{CuK}\alpha$ (40 kV, 40 mA) radiation on a Siemens D5000 Bragg–Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal, 1 mm (0.5°) divergence and antiscatter slits, 0.2 mm receiving slit, and incident- and diffracted-beam Soller slits. The scanning step-size was $0.02^\circ 2\theta$, with a counting time of 20 s/step. The long sample-holder used (43 mm) ensured that the area irra-

diated by the X-ray beam under these conditions was completely contained within the sample at low angles of diffraction.

Rietveld structure refinement

The X-ray powder-diffraction data were refined with the Rietveld program Topas 2.0 (Bruker AXS 2000) using the fundamental parameters approach (Cheary & Coelho 1992). As the powder-diffraction pattern for cobaltarthurite is more similar to that of ojuelaite than to that of arthurite (Jambor *et al.* 2002), starting values for the atom positions, cell dimensions and isotropic displacement parameters were taken from Hughes *et al.* (1996). Neutral scattering factors were used for all atoms. A slight preferred orientation in cobaltarthurite was corrected using the method of spherical harmonics (Järvinen 1993). In spite of careful separation of cobaltarthurite grains from the sample, a few percent of pharmacosiderite and quartz were present in the powder. The contributions of the impurities to X-ray scattering were accounted for by simultaneous refinement of their structures. Starting parameters for the structures of pharmacosiderite and quartz were taken from Buerger *et al.* (1967) and Le Page & Donnay (1976), respectively. The background was refined using a 4th order Chebychev polynomial. After refinement, two humps in the diffraction pattern were not accounted for, a relatively narrow one centered at $2\theta = 8.09^\circ$ (FWHM = $1.52^\circ 2\theta$) and a broad one at $2\theta = 29.42^\circ$ (FWHM = $11.34^\circ 2\theta$). The origin of this excess scattering is unknown, but seems similar to that generated in X-ray powder-diffraction patterns by amorphous or poorly crystalline material, perhaps the result of weathering of the cobaltarthurite. The overall refinement was much improved by using a peak-phase to fit the humps. Attempts to refine the isotropic displacement parameters did not give reasonable values for three of the oxygen

TABLE 1. IDEAL COMPOSITIONS OF MEMBERS OF THE ARTHURITE GROUP, OF GENERAL FORMULA $A^2\text{Fe}^{3+}_2(\text{XO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

Mineral	A	X	Reference
arthurite	Cu^{2+}	As^{5+}	Keller & Hess (1978)*
cobaltarthurite	Co^{2+}	As^{5+}	This study, Jambor <i>et al.</i> (2002)
ojuelaite	Zn^{2+}	As^{5+}	Hughes <i>et al.</i> (1996)*
earlshannonite	Mn^{2+} , Fe^{2+}	P^{5+}	Peacor <i>et al.</i> (1984)
whitmoreite	Fe^{2+}	P^{5+}	Moore <i>et al.</i> (1974)*

* The structure has been determined.

TABLE 2. RESULTS OF ELECTRON-PROBE MICRO-ANALYSES OF COBALARTHURITE

	Average (17)	Range	Number of ions on the basis of ($\text{As}^{5+} + \text{P}^{5+} + \text{S}^{6+}$) = 2.00	
As_2O_5	40.54	39.79 – 41.22	As^{5+}	1.98
P_2O_5	0.12	0.00 – 0.23	P^{5+}	0.01
SO_3	0.13	0.04 – 0.29	S^{6+}	0.01
MnO	0.98	0.65 – 1.16	Sum X	2.00
Fe_2O_3	28.59	27.73 – 29.34	Fe^{3+}	2.01
CoO	7.92	7.08 – 9.00	Mn^{2+}	0.08
NiO	0.29	0.12 – 0.62	Co^{2+}	0.59
CuO	0.32	0.09 – 0.70	Ni^{2+}	0.02
MgO	1.94	1.43 – 2.49	Cu^{2+}	0.02
CaO	0.16	0.08 – 0.26	Mg^{2+}	0.27
H_2O^*	16.04	15.76 – 16.35	Ca^{2+}	0.02
Total	97.03	96.19 – 98.71	Sum A	1.00

* Calculated from stoichiometry, $A^2\text{Fe}^{3+}_2(\text{XO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

atoms [O(1), O(4), OH)], and consequently all displacement parameters were fixed at the values determined by Hughes *et al.* (1996). Miscellaneous information pertaining to the Rietveld refinement of cobaltarthurite is given in Table 3.

RESULTS AND DISCUSSION

Electron-probe micro-analysis and the formula of cobaltarthurite

An average result of 17 electron-probe micro-analyses of cobaltarthurite is given in Table 2, together with the measured range of each element and the numbers of atoms per formula unit. The analyses pertain to material obtained from the full width of the veinlet of cobaltarthurite described by Jambor *et al.* (2002), and, as a consequence, show an expected variation in the abundance of some of the elements. The structural formula, $(\text{Co}_{0.59}\text{Mg}_{0.27}\text{Mn}_{0.08}\text{Ni}_{0.02}\text{Cu}_{0.02}\text{Ca}_{0.02})\text{Fe}^{3+}_{2.01}(\text{As}_{1.98}\text{P}_{0.01}\text{S}_{0.01}\text{O}_4)_2(\text{OH})_{2.04}\cdot 4\text{H}_2\text{O}$, was calculated on the basis of $(\text{As}^{5+} + \text{P}^{5+} + \text{S}^{6+}) = 2.00$ atoms per formula unit (*apfu*), the only part of the formula known with certainty. Although the amount of $(\text{OH})^-$ calculated from charge balance and by assigning an ideal $4\text{H}_2\text{O}$ yields an analytical total that is less than 100% (97.05%), we are confident that this approach leads to the correct formula, as the analyses were done on aggregates of fine-grained and acicular material containing void space, a condition that would cause a lowering of the analytical total. In addition, in spite of using a beam current of only 5 nA, some minor degradation of cobaltarthurite was observed. Despite these experimental challenges, the calculated formula is not significantly different from the ideal one. Our compositions differ from those reported by Jambor *et al.* (2002) in two main respects: (i) higher Mg content, and (ii) no deviation from the stoichiometry of the ideal arthurite-group formula. Although different data-reduction programs may yield different results, especially for As (Jambor *et al.* 2002), the difference in Mg content is likely the result of zoning; in our analyses, Mg content varies by a factor of almost two (Table 2).

TABLE 3. MISCELLANEOUS INFORMATION PERTAINING TO THE STRUCTURE REFINEMENT OF COBALTARTHURITE

<i>a</i> (Å)	10.2694(4)	Space Group	$P2_1/c$
<i>b</i> (Å)	9.6790(3)	<i>Z</i>	2
<i>c</i> (Å)	5.5723(2)	R_{wp}	7.7
β (°)	94.277(2)	R_{exp}	6.2
V (Å ³)	552.33(3)	Goodness of fit	1.2
		R_B	1.7
$R_B = 100 \sum I_{ok} - I_{ck} / \sum I_{ck}$			
$R_{exp} = 100 \{(N - P + C) / \sum w_i (y_{oi})^2\}^{1/2}$			
$R_{wp} = 100 \{(\sum w_i (y_{oi} - y_{ci})^2) / \sum w_i (y_{oi})^2\}^{1/2}$			
GOF = R_{wp} / R_{exp}			

Rietveld refinement and the structure of cobaltarthurite

As there are now five members of the arthurite group with diverse compositions, we propose a formal nomenclature for the three cation sites to avoid confusion stemming from potentially varied elemental substitutions. With reference to the general formula $A^{2+}\text{Fe}^{3+}_2(\text{XO}_4)_2(\text{OH})_2\cdot 4\text{H}_2\text{O}$, the A, Fe^{3+} and X positions are designated in the structure as the *M*(2), *M*(1) and *T* sites, respectively. Results of the Rietveld refinement of the structure of cobaltarthurite are summarized in Table 3 (miscellaneous information), Table 4 (atomic parameters and bond-valence sums), Table 5 (selected interatomic distances) and Figure 1 (Rietveld refinement plot). A projection of the refined structure on (001) is shown in Figure 2a. The standard indicators of agreement of the quality of refinement, $R_{wp} = 7.1$, GOF = 1.2 and $R_B = 1.7$ indicate that it is excellent (Table 2). Although powder-diffraction data are intrinsically less precise than single-crystal diffraction data, our results are completely consistent with the symmetry and stereochemical details of the three previously determined and refined structures of members of the arthurite group, as obtained using data from single-crystal X-ray diffraction (Table 1).

The structure of cobaltarthurite is isostructural with that of whitmoreite (Moore *et al.* 1974), arthurite (Keller & Hess 1978) and ojuelaite (Hughes *et al.* 1996). The arrangement of atoms in cobaltarthurite is characterized by a unique corrugated open sheet of $(\text{Fe}^{3+}\text{O})_6$ octahedra, each of which shares four of its six vertices with adjacent octahedra (Fig. 2b). Vertices with $(\text{OH})^-$ ligands are corner-linked to adjacent octahedra, forming a stepped corner-chain parallel to [001]. These chains are linked into a sheet parallel to (100) by sharing O(1)–O(1) edges with equivalent chains. Above and below the sheet of octahedra are AsO_4 tetrahedra, which share three of four vertices with the octahedra, to form a slab (Fig. 2a). The slabs are joined by isolated $(\text{Co}^{2+}$ –

TABLE 4. ATOMIC PARAMETERS AND BOND-VALENCE SUMS FOR COBALTARTHURITE

Site	<i>x</i>	<i>y</i>	<i>z</i>	¹ B_{iso} (Å ²)	² B.V.S.
<i>M</i> (2)	0	0	0	0.72	1.85
<i>M</i> (1)	0.4554(4)	0.1357(4)	0.3405(9)	0.34	3.00
<i>T</i>	0.2968(3)	0.4293(3)	0.3279(7)	0.35	4.81
O(1)	0.397(1)	0.488(2)	0.118(3)	0.59	2.00
O(2)	0.360(1)	0.491(2)	0.594(3)	0.63	1.72
O(3)	0.148(2)	0.494(1)	0.240(3)	0.87	1.50
O(4)	0.303(1)	0.253(2)	0.323(3)	0.66	1.80
OH	0.540(2)	0.228(2)	0.080(3)	0.61	1.06
OW(1)	0.126(1)	0.909(2)	0.296(3)	1.34	0.25
OW(2)	0.050(1)	0.190(1)	0.150(3)	1.46	0.36

¹Isotropic displacement parameters fixed after Hughes *et al.* (1996).

²Bond-valence sums using parameters from Brown & Altermatt (1985).

O)₆ octahedra, which share two opposite vertices with the remaining vertices of the AsO₄ tetrahedra not shared with the (Fe³⁺-O)₆ octahedra, from above and below each slab.

As the interatomic distances derived from Rietveld refinement are not as precise as those determined from single-crystal structure refinement, a detailed analysis of hydrogen bonding in cobalthurite was not attempted. However, bond-valence sums for cobalthurite (Table 4) are remarkably consistent with those reported by previous investigators. For the bond-valence calculation, the multiple occupancy of the M(2) site was taken into account. Hughes *et al.* (1996) proposed that for ojuelaite, O(1) is not hydrogen bonded, O(2), O(3)

and O(4) are acceptors of hydrogen bonds, and OW1 and OW2 are donors of hydrogen bonds, a conclusion similar to that proposed by Moore *et al.* (1974) for hydrogen bonding in the whitmoreite structure. Our results are in agreement with these findings.

An unconstrained refinement of the occupancies of the T, M(1) and M(2) sites shows that they are fully occupied by the expected substituent cations. In particular, refinement of the variably occupied M(2) site for electron occupancy yielded 23.2 electrons, in good agreement with 22.8 electrons calculated from results of the electron-probe micro-analyses (Table 2).

CONCLUSIONS

Taking into account the effects of variable composition, cobalthurite is isostructural with the known members of the arthurite group. From the results of both the Rietveld refinement and electron-probe micro-analyses, we find no evidence of significant deviation from the ideal formula, A²⁺Fe³⁺₂(XO₄)₂(OH)₂•4H₂O, where A²⁺ = Cu, Fe, Mn, Zn, Co, Ni, Mg, Ca; X = As⁵⁺, P⁵⁺, S⁶⁺.

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TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN COBALTARTHURITE

M(2)-O(3)	×2	2.175(19)	M(1)-O(1)	2.080(18)
M(2)-OW(1)	×2	2.204(15)	M(1)-O(1)	2.081(16)
M(2)-OW(2)	×2	<u>2.066(14)</u>	M(1)-O(2)	2.039(17)
<M(2)-O>		2.15	M(1)-O(4)	1.931(14)
			M(1)-OH	2.028(17)
T-O(1)		1.712(18)	M(1)-OH	<u>1.963(19)</u>
T-O(2)		1.684(18)	<M(1)-O>	2.02
T-O(3)		1.690(16)		
T-O(4)		<u>1.710(15)</u>		
<T-O>		1.70		

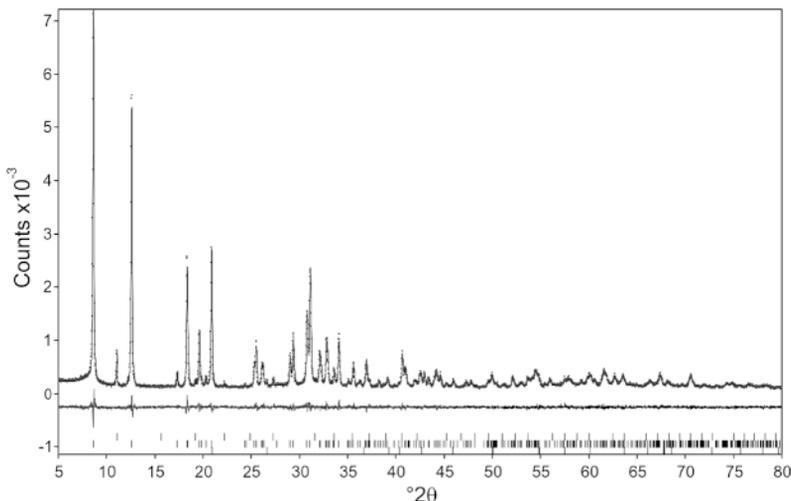


FIG. 1. Rietveld refinement plot for cobalthurite. Dots: observed intensity at each step, line: calculated pattern, line below: difference between observed and calculated intensities, vertical bars: positions of all Bragg reflections for pharmacosiderite, cobalthurite, quartz (from top to bottom).

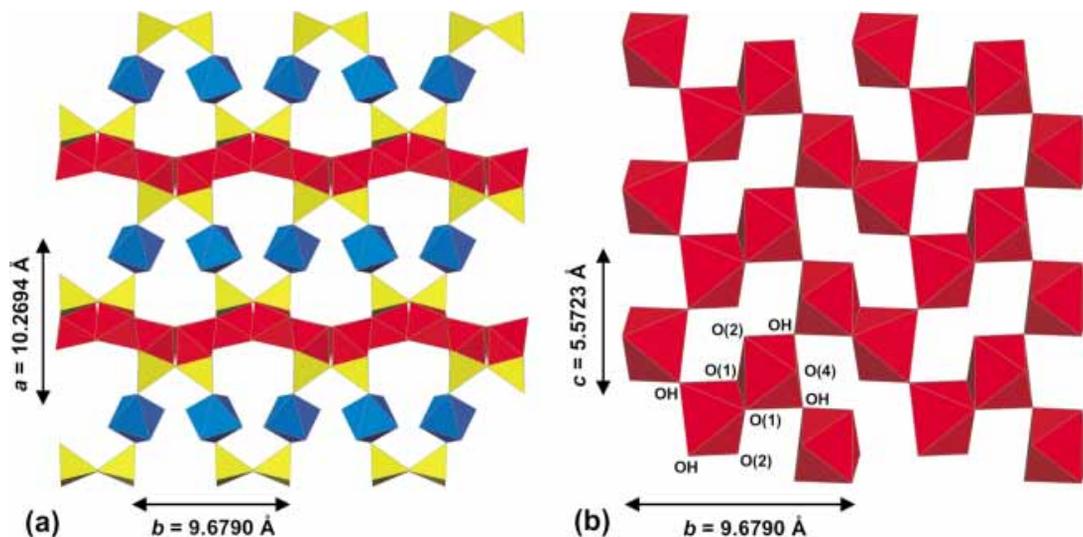


FIG. 2. The crystal structure of cobaltarthurite: (a) projection on (001); (b) the $\text{Fe}^{3+}\text{-O}$ open sheet projected on (100). For the ideal formula $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, blue, red and yellow polyhedra represent $(\text{Co}^{2+}\text{-O})_6$ octahedra, $(\text{Fe}^{3+}\text{-O})_6$ octahedra, and $(\text{As-O})_4$ tetrahedra, respectively.

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