

## COBALTARTHURITE, $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , A NEW MEMBER OF THE ARTHURITE GROUP

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### ABSTRACT

Cobaltarthurite, of ideal end-member formula  $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , is a new Co-dominant member of the arthurite group and is named to reflect that relationship. The new species occurs predominantly as coalesced pellet-like spheres, up to 1½ mm across, that consist of straw-yellow to dark brown radial aggregates of fibrous crystals only a few micrometers in width. The mineral has a vitreous to silky luster, is brittle, translucent, nonfluorescent, has a hardness of 3½–4, a white to light brown streak, and is readily soluble in HCl. Cobaltarthurite is biaxial positive,  $\alpha$  1.741,  $\beta$  1.762,  $\gamma$  1.797, 2V (calc.) 77°, with parallel extinction; the pleochroism is distinct, from almost colorless to medium yellow. Electron-microprobe analyses of yellow and dark brown material gave similar compositions, with the latter corresponding to  $(\text{Co}_{0.50}\text{Mg}_{0.12}\text{Fe}^{3+}_{0.11}\text{Mn}_{0.08}\text{Cu}_{0.01}\square_{0.11})_{\Sigma 0.93}\text{Fe}^{3+}_2[(\text{AsO}_4)_{1.95}(\text{PO}_4)_{0.04}(\text{SO}_4)_{0.01}]_{\Sigma 2.00}(\text{OH})_{1.74} \cdot 4\text{H}_2\text{O}$ , for which  $D_{\text{calc}}$  is 3.179 g/cm<sup>3</sup> for Z = 2; the measured density is 3.22(2) g/cm<sup>3</sup>. Indexing of the X-ray powder pattern, which is similar to those of the other members of the arthurite group, gave a monoclinic cell with  $a$  10.27,  $b$  9.72,  $c$  5.545 Å,  $\beta$  94.46°. The strongest six lines of the powder pattern [ $d$  in Å( $I$ )( $hkl$ )] are: 10.2(95)(100), 7.04(100)(110), 4.81(65)(001), 4.24(60)(111), 2.89(25)(221), and 2.87(55)(311). The mineral is associated with pharmacosiderite, olivenite, conicalcrite, jarosite, arseniosiderite, and several other products of oxidation in a near-surface, sulfide-depleted lens near Mazarrón, in the Province of Murcia, southeastern Spain.

*Keywords:* cobaltarthurite, arthurite group, new mineral species, arsenate, X-ray data, infrared spectra, Raman spectra, Mazarrón, Spain.

### SOMMAIRE

La cobaltarthurite, dont la formule idéale serait  $\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , est un membre nouvellement défini du groupe de l'arthurite à dominance de cobalte; son nom reflète cette relation. La nouvelle espèce se présente surtout sous forme de sphères jusqu'à 1½ mm de diamètre en coalescence, faits d'aggrégats fibroradiés jaune paille à brun foncé, les fibres ayant une largeur de quelques micromètres. Le minéral montre un éclat vitreux à soyeux, est cassant, translucide, nonfluorescent, possède une dureté 3½ à 4 et une rayure brun pâle, et est facilement dissoute dans l'acide chlorhydrique. La cobaltarthurite est biaxe positive,  $\alpha$  1.741,  $\beta$  1.762,  $\gamma$  1.797, 2V (calc.) 77°, avec une extinction parallèle; le pléochroïsme est distinct, de presque incolore jusqu'à jaune moyen. Les analyses à la microsonde électronique des matériaux jaune et brun ont donné des résultats semblables; dans le cas des fibres brunes, la composition est:  $(\text{Co}_{0.50}\text{Mg}_{0.12}\text{Fe}^{3+}_{0.11}\text{Mn}_{0.08}\text{Cu}_{0.01}\square_{0.11})_{\Sigma 0.93}\text{Fe}^{3+}_2[(\text{AsO}_4)_{1.95}(\text{PO}_4)_{0.04}(\text{SO}_4)_{0.01}]_{\Sigma 2.00}(\text{OH})_{1.74} \cdot 4\text{H}_2\text{O}$ , pour laquelle la densité calculée est 3.179 g/cm<sup>3</sup> et Z = 2; la densité mesurée est 3.22(2) g/cm<sup>3</sup>. L'indexation du spectre de diffraction obtenu sur poudre, qui ressemble ceux des autres membres du groupe de l'arthurite, a donné une maille monoclinique,  $a$  10.27,  $b$  9.72,  $c$  5.545 Å,  $\beta$  94.46°. Les cinq raies les plus intenses [ $d$  en Å( $I$ )( $hkl$ )] sont: 10.2(95)(100), 7.04(100)(110), 4.81(65)(001), 4.24(60)(111), 2.89(25)(221), et 2.87(55)(311). Lui sont associées pharmacosidérite, olivénite,

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conichalcite, jarosite, arséniosidérite, et plusieurs autres produits d'oxydation d'une lentille à faible teneur en sulfures près de Mazarrón, province de Murcia, dans le sud-est de l'Espagne.

(Traduit par la Rédaction)

*Mots-clés:* cobaltarthurite, groupe de l'arthurite, nouvelle espèce minérale, arséniate, diffraction X, spectres infra-rouges, spectres de Raman, Mazarrón, Espagne.

## INTRODUCTION

The arthurite group (Anthony *et al.* 2000, Mandarinio 1999) or whitmoreite group (Gaines *et al.* 1997) consists of arsenates and phosphates with the general formula  $A\text{Fe}^{3+}_2(\text{TO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , wherein *A* represents Cu and Zn in the two previously known arsenate members, and  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the two known phosphate members. Arthurite, variously written as  $\text{CuFe}^{3+}_2(\text{AsO}_4)_2(\text{O},\text{OH})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{CuFe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , was the first described mineral of the group (Davis & Hey 1964, 1969). The Zn-dominant analogue of arthurite is ojuelaite (Cesbron *et al.* 1981), and here we describe the third arsenate member. It is the Co-dominant analogue and is accordingly named cobaltarthurite to signify that relationship. The new mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The type material, catalogued as NMNMC 83399, is kept at the Canadian Museum of Nature, Ottawa.

## OCCURRENCE AND PROPERTIES

The specimens of cobaltarthurite were collected from the Dolores showing, an oxidized near-surface lens about  $10 \times 2 \times 0.2$  m. The showing is located near Pastrana, a village about 10 km east of Mazarrón in the Province of Murcia, southeastern Spain. The Mazarrón district, although currently lacking a producing mine, has for centuries been an important source of Pb–Zn–Ag ores, mainly from Miocene hydrothermal stockwork veins within Paleozoic volcanic and subvolcanic rocks (Arribas & Tosdal 1994). Also present within the district are unrelated Cu prospects, including the Dolores, that consist chiefly of arsenopyrite, tennantite, and chalcopyrite in quartz–carbonate veins. Although no primary sulfides remain in the Dolores lens, the Cu- and As-rich oxidized assemblage is in accord with the presumed primary mineralogy. The source of the Co to form cobaltarthurite may have been cobaltoan arsenopyrite.

Cobaltarthurite occurs as globular to pellet-like aggregates, with each unit consisting of a compact mass of yellowish, radial fibers and dark brown, non-fibrous, microscopic intergrowths. Color zoning is megascopically prominent, and typically each globule grades from a straw-yellow exterior to a dark brown core. No significant compositional difference between the two color

types has been detected by electron-microprobe analysis. Tufts of minute, divergent needles have also been observed, but they are rare.

Individual globules are up to  $1\frac{1}{2}$  mm across, but most are in the range  $\frac{1}{2}$ –1 mm. The largest surface coating is about  $0.7 \times 1.4$  cm. The mineral also occurs as a fill in fractures, and the largest of these veinlets, about 0.4 cm wide and 1.4 cm long, was used to extract material for the Rietveld refinement (Raudsepp & Pani 2002). Individual fibers within the globules and tufts are up to 75  $\mu\text{m}$  long; the fibers are roughly equant in cross-section and are only about 2–3  $\mu\text{m}$  wide. The mineral is translucent and has a vitreous luster (silky for the tufts). The streak is white for yellowish grains, and is pale brown for the dark material. The mineral is brittle, with no cleavage or parting observed, and no fluorescence in ultraviolet light. Although the globules seem to be extremely soft, the effect is attributable to displacement or rupture of the fibers; the Mohs hardness is substantially greater than that of the associated pharmacosiderite ( $H = 2\frac{1}{2}$ ) and was determined to be roughly 3 $\frac{1}{2}$ –4, similar to that of scorodite. Cobaltarthurite is readily soluble in 1:1 HCl, which rapidly turns yellowish.

In transmitted light, the fibers have a parallel extinction and are length slow. The mineral is biaxial positive,  $\alpha$  1.741,  $\beta$  1.762,  $\gamma$  1.797,  $2V_{\text{calc}} 77^\circ$ . By analogy with other members of the group, *Z* is approximately equal to *c*. The mineral is distinctly pleochroic, with *X* almost colorless, *Z* medium yellow, and  $Z > X, Y$ .

Oxidation of the primary sulfides at the type locality has resulted in a varied assemblage of secondary minerals, among which are conichalcite, olivenite, pharmacosiderite, jarosite, arseniosiderite, scorodite, malachite, azurite, chlorargyrite, mixite, and lavendulan. These are described in more detail elsewhere (Sainz de Baranda *et al.*, in prep.). The most consistent association of cobaltarthurite is with pharmacosiderite, the latter occurring both along fracture walls and interstitially among the cobaltarthurite pellets (Fig. 1).

## CHEMICAL COMPOSITION

Numerous electron-microprobe analyses of cobaltarthurite samples were made at the University of Barcelona, the University of British Columbia, and at CANMET, Ottawa, mainly because of an inability to obtain stoichiometric compositions from the analytical results. Use of a conventional ZAF correction program

gave high values for As, which in turn decreased the occupancy at the A site because formulas were calculated on the basis of  $TO_4 = 2$ . However, use of either a modified ZAF program or the PAP program gave lower As values and similar results for both programs. The

TABLE 1. COMPOSITION OF COBALTARTHURITE

Constituent	Yellow Fibrous		Brown Massive	
MgO wt. %	0.59	0.52 – 0.66	0.89	0.75 – 0.98
MnO	1.04	0.91 – 1.11	1.14	1.04 – 1.22
CoO	7.15	6.78 – 7.55	7.06	6.78 – 7.34
CuO	0.04	0.00 – 0.09	0.20	0.05 – 0.35
Fe <sub>2</sub> O <sub>3</sub>	32.02	31.44 – 32.68	31.88	31.05 – 32.69
As <sub>2</sub> O <sub>3</sub>	44.23	43.34 – 45.47	42.57	41.78 – 43.54
P <sub>2</sub> O <sub>5</sub>	0.45	0.19 – 0.65	0.56	0.40 – 0.66
SO <sub>3</sub>	0.08	0.04 – 0.10	0.07	0.04 – 0.11
[H <sub>2</sub> O]	16.63		16.64	
Total	102.23		101.01	

The average composition and the range of concentrations are given for the two variants. Total Fe as Fe<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O calculated. Each average is for 10 spots analyzed by J.H.G. Laflamme at 20 kV, 20 nA, and counting times of 20 to 40 s; standards and X-ray lines used were Fe<sub>2</sub>O<sub>3</sub> (FeK $\alpha$ ), Co metal and Cu metal (K $\alpha$ ), MgAl<sub>2</sub>O<sub>4</sub> (MgK $\alpha$ ), MnTiO<sub>3</sub> (MnK $\alpha$ ), InAs (AsL $\alpha$ ), apatite (PK $\alpha$ ), and PbSO<sub>4</sub> (SK $\alpha$ ).

major difference between the compositional data reported here (Table 1) and those obtained from the Rietveld refinement (Raudsepp & Pani 2002) is for Mg, the content of which is sufficiently low that the definition of the mineral is unaffected. The results in Table 1 correspond to  $(Co^{2+}_{0.49}Mg_{0.07}Mn_{0.07}Cu_{0.04}Fe^{3+}_{0.04}\square_{0.04})\Sigma_{0.71}Fe^{3+}_2[(AsO_4)_{1.95}(PO_4)_{0.04}(SO_4)_{0.01}]\Sigma_{2.00}(OH)_{1.42}\cdot 4H_2O$  for the yellow fibrous material, and to  $(Co^{2+}_{0.50}Mg_{0.12}Fe^{3+}_{0.11}Mn_{0.08}Cu_{0.01}\square_{0.11})\Sigma_{0.93}Fe^{3+}_2[(AsO_4)_{1.95}(PO_4)_{0.04}(SO_4)_{0.01}]\Sigma_{2.00}(OH)_{1.74}\cdot 4H_2O$  for the dark brown, non-fibrous intergrowth. The  $\square$  signifies a vacancy, to compensate for the arbitrarily assumed presence of ferric rather than ferrous Fe at the A site. The close association of cobaltarthurite and pharmacosiderite, the latter containing only trivalent Fe, supports the assumption. As well, Moore *et al.* (1974) reported substantial substitution of Fe<sup>3+</sup> for Fe<sup>2+</sup> at the A site of whitmoreite.

The ideal end-member formula of cobaltarthurite is taken to be  $Co^{2+}Fe^{3+}_2(AsO_4)_2(OH)_2\cdot 4H_2O$ . Calculation of the empirical formula on the basis of  $TO_4 = 2$  is preferred on crystal-structure grounds; if, however, the calculation is done for 14 oxygen atoms, and assuming that all Fe is trivalent and each Fe<sup>3+</sup> atom has a corresponding vacancy, the empirical formula of the yellow fibrous

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR COBALTARTHURITE

$I_{est}$	$d_{meas}$	$d_{calc}$	$hkl$	$I_{est}$	$d_{meas}$	$d_{calc}$	$hkl$	$I_{est}$	$d_{meas}$	$d_{calc}$	$hkl$
95	10.2	10.239	100	<5	2.143	2.148	$\bar{4}21$	<5	1.652	1.654	441
100	7.04	7.049	110	<5	2.118	2.122	331			1.653	$\bar{3}13$
65	4.81	4.805	011			2.121	222	<5	1.641	1.645	$\bar{3}42$
20	4.51	4.530	210	5	2.048	2.048	500			1.644	$\bar{6}11$
60	4.24	4.241	111			2.047	421	<5B	1.587	1.590	052
<5	3.63	3.628	$\bar{2}11$	<5	2.029	2.030	$\bar{3}22$			1.587	502
15	3.50	3.495	$\bar{1}21$			2.025	312			1.585	$\bar{3}23$
10	3.41	3.413	300	<5	1.998	2.004	510	<5	1.559	1.561	152
20B	3.05	3.047	$\bar{2}21$	<5	1.968	1.955	402			1.559	$\bar{2}33$
25	2.89	2.902	221	<5	1.918	1.917	412			1.555	061
55	2.87	2.876	$\bar{3}11$	<5	1.901	1.906	232	5	1.538	1.542	$\bar{1}61$
10	2.78	2.793	320			1.905	322			1.538	$\bar{2}52$
15	2.720	2.724	$\bar{1}31$	5	1.822	1.826	521			1.534	$\bar{4}13$
		2.722	$\bar{1}02$			1.825	042	<5	1.525	1.523	442
<5	2.662	2.670	131			1.817	250	5	1.502	1.505	$\bar{6}02$
		2.659	012	<5	1.780	1.781	142			1.500	233
10	2.619	2.621	$\bar{1}12$			1.779	412			1.500	252
		2.618	102	5	1.749	1.749	$\bar{2}13$	<5	1.479	1.483	$\bar{6}31$
5	2.514	2.515	$\bar{2}02$			1.748	521			1.480	$\bar{4}23$
<5	2.470	2.475	410			1.748	242			1.479	261
10	2.430	2.435	$\bar{2}12$	<5	1.726	1.731	530	<5	1.462		
		2.431	321			1.723	023	<5	1.407		
		2.430	040	<5	1.702	1.706	600	5	1.387		
<5	2.358	2.364	140			1.706	441	<5	1.373		
		2.357	202			1.696	422	5	1.332		
5	2.293	2.290	212	5	1.678	1.681	610				
10	2.209	2.205	$\bar{3}31$			1.679	123				
						1.674	432				

Debye-Scherrer camera, diameter 114.6 mm, CoK $\alpha$  radiation, intensities visually estimated, no internal standard. Indexed with  $a$  10.27,  $b$  9.72,  $c$  5.545 Å,  $\beta$  94.46°. B: broad.

TABLE 3. SUMMARY OF SOME PROPERTIES OF THE ARTHURITE GROUP

	arthurite	ojuelaite	cobaltarthurite	whitmoreite	earlshannonite
	$\text{CuFe}^{3+}_{-1}(\text{AsO}_4)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$\text{ZnFe}^{3+}_2(\text{AsO}_4)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	$\text{Mn}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
<i>a</i> (Å)	10.189	10.237	10.27	10.00	9.910
<i>b</i> (Å)	9.649	9.662	9.72	9.73	9.669
<i>c</i> (Å)	5.598	5.562	5.545	5.471	5.455
$\beta$ (°)	92.16	94.36	94.46	93.8	93.95
S.G.	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>D</i> <sub>meas</sub>	3.376	3.39	3.22	2.87	2.90
<i>D</i> <sub>calc</sub>	3.376	3.39	3.179–3.248	2.85	2.92
H	not given	3	3½–4	3	3–4
Color	apple green to bluish green	greenish yellow	yellow to dark brown	tan, dark brown, greenish brown	reddish brown to bright yellow
$\alpha$	1.736–1.746	1.696	1.741	1.676	1.696
$\beta$	1.767–1.774	1.730	1.762	1.725	1.745
$\gamma$	1.796–1.806	1.798	1.797	1.745	1.765
2 <i>V</i> (°)	~90	73	77 (calc)	60–65	64
Sign	(+) or (–)	(+)	(+); length slow	(–)	(–)
<i>X</i>	pale yellow to green	yellow	almost colorless	<i>X</i> , <i>Y</i> light greenish brown	<i>X</i> = <i>Y</i> light yellow-brown
<i>Y</i>	grass green		—		
<i>Z</i>	yellow-green to olive green		medium yellow	dark greenish brown	yellow-brown
Orientation	<i>Z</i> > <i>Y</i> > <i>X</i> <i>Z</i> : <i>c</i> = 10°	<i>Z</i> = <i>X</i> > <i>Y</i> <i>X</i> = <i>b</i> , <i>Z</i> = <i>c</i>	<i>Z</i> > <i>X</i> , <i>Y</i> <i>Z</i> ≈ <i>c</i>	<i>Z</i> > <i>X</i> , <i>Y</i> <i>X</i> = <i>a</i> , <i>Y</i> = <i>b</i> , <i>Z</i> = <i>c</i>	<i>Z</i> > <i>X</i> , <i>Y</i> <i>Z</i> = <i>c</i>
Habit	prismatic to acicular	fibrous [001]	fibrous	acicular [001], fans, sprays	radial prismatic, elongate [001]

Principal sources: arthurite: Davis & Hey (1964), Keller & Hess (1978), ojuelaite: Hughes *et al.* (1996), Cesbron *et al.* (1981), whitmoreite: Moore *et al.* (1974), and earlshannonite: Peacor *et al.* (1984).

material is  $(\text{Co}_{0.51}\text{Fe}^{3+}_{0.15}\square_{0.15}\text{Mg}_{0.12}\text{Mn}_{0.09}\text{Cu}_{0.01})_{\Sigma 1.03}[(\text{AsO}_4)_{1.99}(\text{PO}_4)_{0.04}]_{\Sigma 2.03}(\text{OH})_{1.82} \cdot 4.05\text{H}_2\text{O}$ . For the two preceding empirical formulas calculated with  $TO_4 = 2$ ,  $D_{\text{calc}}$  is 3.248 and 3.179 g/cm<sup>3</sup> for  $Z = 2$ ; a measured density of 3.22(2) g/cm<sup>3</sup> was obtained by suspension of the mineral in heavy liquids. The various formulas give superior to excellent Gladstone–Dale compatibilities (Mandarino 1981).

For comparative purposes, an electron-microprobe analysis of arthurite from Majuba Hill, Pershing County, Nevada, gave a composition corresponding to  $(\text{Cu}_{0.97}\text{Mg}_{0.01}\Sigma_{0.98}\text{Fe}^{3+}_{1.78}[(\text{AsO}_4)_{1.97}(\text{PO}_4)_{0.02}(\text{SO}_4)_{0.01}](\text{OH})_{1.31} \cdot 4.83\text{H}_2\text{O}$ . In the analysis, which was made at the University of Barcelona under the same conditions as for other analyses of cobaltarthurite, the amount of H<sub>2</sub>O is obtained by difference from 100 wt.%. The low (OH) required to achieve charge balance is a reflection of the low content of Fe<sup>3+</sup>, whereas in cobaltarthurite the low (OH) is a consequence of the low total cations in A.

To investigate whether part of the Co in cobaltarthurite may be trivalent, polished sections of erythrite  $[\text{Co}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$  from Bou Azzer, Morocco, and heterogenite  $[\text{Co}^{3+}\text{O}(\text{OH})]$  from Mindigi, Democratic Republic of Congo, were analyzed to determine whether

a wavelength shift related to the valence state of Co is present. No shift for the CoL lines was detected. The  $K_{\alpha}/K_{\beta}$  value for brown cobaltarthurite is close to that in heterogenite, whereas the ratio in yellow cobaltarthurite is intermediate to those of heterogenite and erythrite; the results, however, are inconclusive because  $K_{\alpha}/K_{\beta}$  can be affected both by oxidation state and the bonding environment (Armstrong 1999).

#### X-RAY DATA

The fibers of cobaltarthurite are too thin for conventional single-crystal X-ray study. X-ray powder mounts of the yellow and dark brown parts of a globule were prepared while viewing the material with a binocular microscope. No difference in the resulting Debye–Scherrer patterns was discernible. The pattern of cobaltarthurite was indexed on the basis of its similarity to those of the other members of the arthurite group. The resulting unit-cell dimensions (Table 2) are in good agreement with results obtained from the Rietveld refinement (Raudsepp & Pani 2002) and are similar to the cell dimensions of the other members of the arthurite group (Table 3).

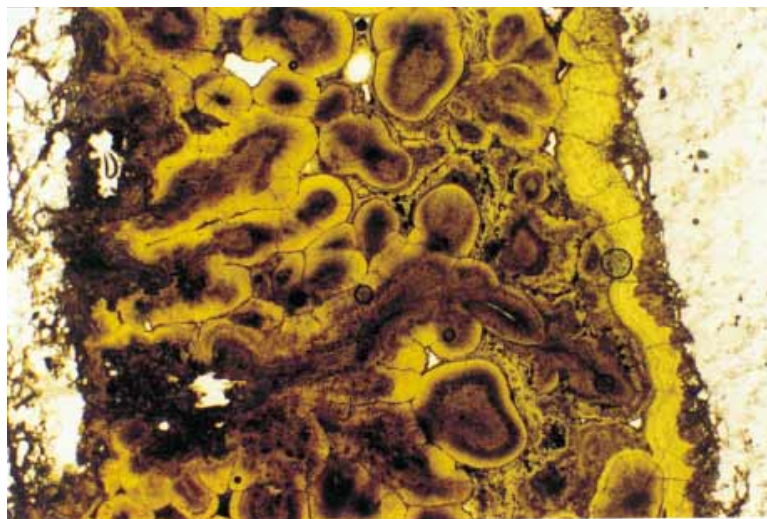


FIG. 1. Cobaltarthurite in plane-polarized transmitted light, showing the pellet-like character and color zoning in a wide veinlet. The colorless margins are the quartzite wallrock, and the continuous yellow band along the right margin of the veinlet is pharmacosiderite, which also is present in small amounts interstitially among the pellets. Width of field of view: 5.1 mm.

#### INFRARED AND RAMAN DATA

The infrared spectra of yellow and brown cobaltarthurite were obtained with a Bomen MB-120 microscope – spectrometer with a detection range of 775 to 4000  $\text{cm}^{-1}$ . Each sample consisted of coherent, uncrushed, subparallel fibrous material, about 0.02 mm thick and 1 mm long, mounted perpendicular to the unpolarized-light source. The spectra (Fig. 2) are similar for both varieties, with minor variations at low wavelengths. A strong, broad absorption band at about 3200  $\text{cm}^{-1}$  is assignable to OH-stretching vibrations, and a strong, sharp band at 1659  $\text{cm}^{-1}$  indicates the presence of structural  $\text{H}_2\text{O}$ . The origin of the sharp band at 1042  $\text{cm}^{-1}$  is uncertain, but similar bands at 1055 and 1040  $\text{cm}^{-1}$  in arthurite were tentatively assigned to As–OH interactions by Keller & Hess (1978). The bands at 894 and 830  $\text{cm}^{-1}$  in cobaltarthurite are attributable to As–O stretching vibrations (Myneni *et al.* 1998).

Laser-Raman spectra (Fig. 3) were obtained with a Jobin Yvon T64000 instrument, using an Ar laser and a CCD detector. The spectra are from the same polished sections of arthurite and cobaltarthurite that had been analyzed by electron microprobe. In the high-frequency region, not included in Figure 3, cobaltarthurite has three absorption bands at 3186, 3250, and 3557  $\text{cm}^{-1}$  in the OH-stretching region, with the last band tentatively assignable to  $M$ –OH stretching, as in tyrolite (Kloprogge & Frost 2000). The equivalent bands in arthurite are at

3163, 3239, and 3496  $\text{cm}^{-1}$ , but a fourth band appears at 3307  $\text{cm}^{-1}$ . The reason for this difference is not known.

Both arthurite and cobaltarthurite responded poorly in the  $\text{H}_2\text{O}$  band region from 1850 to 1450  $\text{cm}^{-1}$ , which is commonly of low sensitivity in Raman spectroscopy and is not shown in Figure 3. A weak band at about 1675  $\text{cm}^{-1}$  appears for arthurite, whereas in cobaltarthurite an extremely broad and weak band extends from about 1750 to 1550  $\text{cm}^{-1}$ . In the low-frequency region from 0 to 1200  $\text{cm}^{-1}$  (Fig. 3), peaks for the As–O stretching mode form a cluster from 950 to 750  $\text{cm}^{-1}$ ; on the basis of data in Myneni *et al.* (1998), the assignments for the bands at 907, 846, 816, and 779  $\text{cm}^{-1}$  in cobaltarthurite are, respectively,  $\nu_{1(s)}$  uncomplexed As–O,  $\nu_{3(as)}$  uncomplexed As–O,  $\nu_{1(s)}$  complexed As–OX, and  $\nu_{3(as)}$  complexed As–OX, where the subscripts *s* and *as* indicate symmetric and asymmetric stretching, and X is  $\text{H}^+$ , a cation, or  $\text{H}_2\text{O}$ . The region from 550 to 300  $\text{cm}^{-1}$  includes the  $M$ –O and  $M$ –OH stretching and As–O bending vibrations (Kloprogge & Frost 1999). The region at <300  $\text{cm}^{-1}$  probably corresponds to  $M$ –OH,  $M$ –O–As, and at the lowest frequencies, O– $M$ –O(H) bending and lattice modes.

#### ACKNOWLEDGEMENTS

We are grateful to mineral collector A. Barahonas, who collected and provided the specimens. J.D. Grice of the Canadian Museum of Nature helped with the

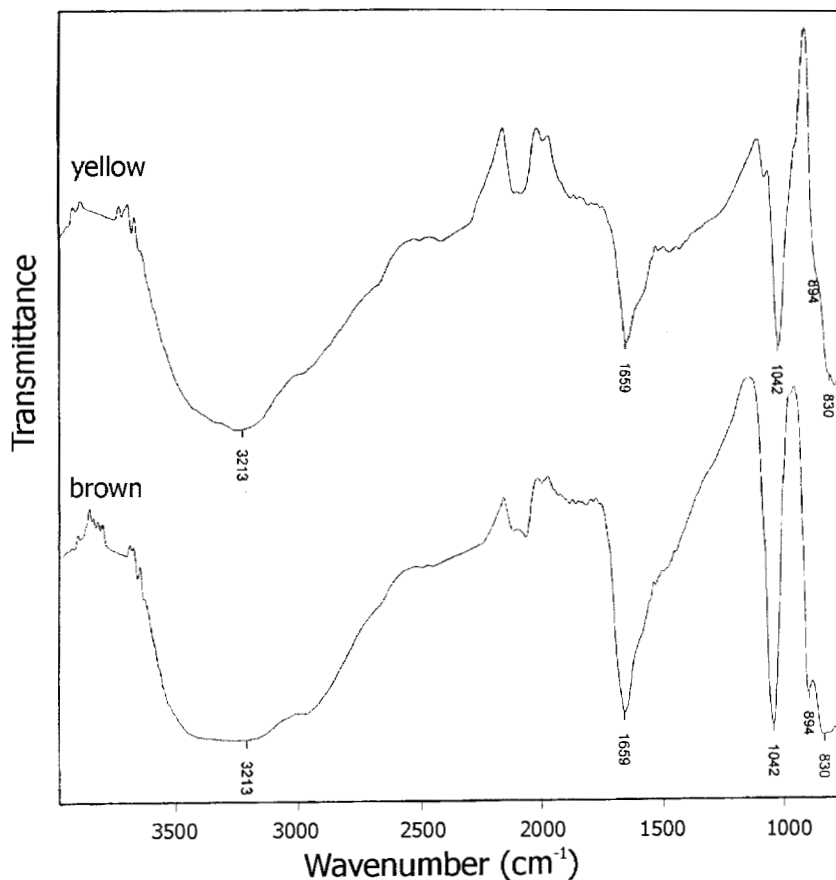


FIG. 2. Infrared spectra of the yellow and brown varieties of cobaltarthurite.

optical study, and P. Carrière, J.H.G. Laflamme, and B. Pemberton provided technical assistance. We are indebted to Serveis Científicotècnics of the University of Barcelona for providing the microbeam, spectroscopic, and XRD instrumentation, as well as the expertise, that helped to characterize the new mineral.

R.F. Martin kindly facilitated the appearance of this paper in the issue dedicated to Louis Cabri. Louis and the first author were for many years coworkers in the mineralogy group at CANMET, and during part of that time we also fruitfully collaborated as co-editors of *The Canadian Mineralogist*. We thank U. Kolitsch, P.A. Williams, J.A. Mandarino, and R.F. Martin for comments and reviews that helped to improve the final manuscript.

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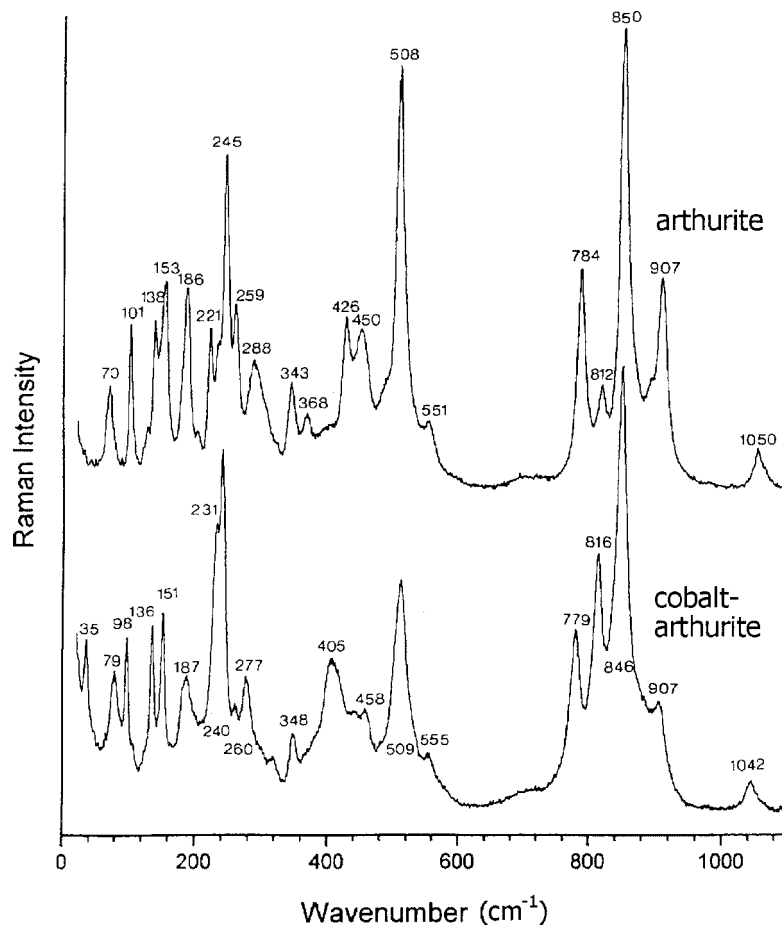


FIG. 3. Raman spectra of polished sections of cobaltarthurite and arthurite.

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*Received November 24, 2001, revised manuscript accepted February 22, 2002.*