

## RRUFFITE, $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , A NEW MEMBER OF THE ROSELITE GROUP, FROM TIERRA AMARILLA, CHILE

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### ABSTRACT

A new mineral species, ruffite, ideally  $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , has been found in the oxidation zone of the Cu–As orebody in the Maria Catalina mine, Tierra Amarilla, Chile. It is a secondary mineral and occurs in granular or blocky aggregates and druses. Associated minerals include quartz, barite, mansfieldite, alumopharmacosiderite, conichalcite, metazeunerite, and barahonite-(Al). Ruffite is pale or light blue, transparent with white streak and vitreous luster. It is brittle, has a Mohs hardness of ~3 and a perfect cleavage on {010}, and is twinned on (100). The measured and calculated densities are 3.79(3) and 3.77(2) g/cm<sup>3</sup>, respectively. Ruffite is insoluble in water, acetone, and hydrochloric acid. Optically, it is biaxial (–), with  $\alpha$  1.725(1),  $\beta$  1.734(1),  $\gamma$  1.740(1),  $2V_{\text{meas}}$  80(2)°,  $Y = \mathbf{b}$ ,  $X \wedge \mathbf{c}$  49°, and it does not fluoresce under long- or short-wave ultraviolet light. The dispersion is weak, with  $r < v$ . An electron-microprobe analysis yielded the empirical formula  $\text{Ca}_{2.01}\text{Cu}_{1.01}(\text{AsO}_4)_{2.02} \cdot 1.9\text{H}_2\text{O}$ . Ruffite, isostructural with roselite, is monoclinic, with space group  $P2_1/c$  and unit-cell parameters  $a$  5.8618 (2),  $b$  12.7854 (5),  $c$  5.7025 (2) Å,  $\beta$  109.425(2)°, and  $V$  403.05(3) Å<sup>3</sup>. Its structure is characterized by isolated  $\text{CuO}_4(\text{H}_2\text{O})_2$  octahedra that are linked by corner-sharing with  $\text{AsO}_4$  tetrahedra to form the kröhnkite-type chains parallel to the  $\mathbf{c}$  axis. These chains are linked together by large Ca cations and hydrogen bonding. Owing to the strong Jahn–Teller effect, the  $\text{MO}_4(\text{H}_2\text{O})_2$  octahedron in ruffite is the most distorted of all known roselite-group minerals ( $M = \text{Cu, Co, Mn, Mg, and Zn}$ ) in terms of the quadratic elongation of the octahedra. The Raman spectra of ruffite resemble those of arsenate minerals of the roselite group.

*Keywords:* ruffite, roselite, arsenate, crystal structure, X-ray diffraction, Raman spectra, Tierra Amarilla, Chile.

### SOMMAIRE

Nous décrivons une nouvelle espèce minérale, la ruffite, de formule idéale  $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , dans la zone d'oxydation d'un minerai de Cu–As à la mine Maria Catalina, Tierra Amarilla, au Chili. Il s'agit d'un minéral secondaire qui se présente en agrégats granulaires ou en blocs, ainsi que dans des cavités. Lui sont associés quartz, barite, mansfieldite, alumopharmacosidérite, conichalcite, métazeunerite, et barahonite-(Al). La ruffite est bleu pâle, transparente avec une rayure blanche et un éclat vitreux. Elle est cassante, possède une dureté de Mohs d'environ 3 et un clivage {010} parfait, et est maclée sur (100). Les densités mesurée et calculée sont 3.79(3) et 3.77(2) g/cm<sup>3</sup>, respectivement. La ruffite est insoluble dans l'eau, l'acétone, et l'acide chlorhydrique. Elle est biaxe négative, avec  $\alpha$  1.725(1),  $\beta$  1.734(1),  $\gamma$  1.740(1),  $2V_{\text{mes}}$  80(2)°,  $Y = \mathbf{b}$ , et  $X \wedge \mathbf{c}$  49°; elle ne montre aucune fluorescence en lumière ultraviolette en longueurs d'onde longue ou courte. La dispersion est faible, avec  $r < v$ . Une analyse effectuée avec une microsonde électronique a mené à la formule empirique  $\text{Ca}_{2.01}\text{Cu}_{1.01}(\text{AsO}_4)_{2.02} \cdot 1.9\text{H}_2\text{O}$ . La ruffite, isostructurale avec la roselite, est monoclinique, groupe spatial  $P2_1/c$ , avec les paramètres réticulaires  $a$  5.8618 (2),  $b$  12.7854 (5),  $c$  5.7025 (2) Å,  $\beta$  109.425(2)°, et  $V$  403.05(3) Å<sup>3</sup>. Sa structure contient des octaèdres  $\text{CuO}_4(\text{H}_2\text{O})_2$  isolés liés par partage de coins avec des tétraèdres  $\text{AsO}_4$  pour former des chaînes de type kröhnkite parallèles à l'axe  $\mathbf{c}$ . Ces chaînes sont connectées l'une à l'autre par des cations Ca et par liaisons hydrogènes. A cause de la forte influence de l'effet Jahn–Teller, l'octaèdre  $\text{MO}_4(\text{H}_2\text{O})_2$  dans la ruffite est le plus déformé de tous les minéraux faisant partie de groupe de la roselite ( $M = \text{Cu, Co, Mn, Mg, et Zn}$ ) en termes de l'allongement quadratique de l'octaèdre. Les spectres de Raman de la ruffite ressemblent à ceux des minéraux arsenatés du groupe de la roselite.

(Traduit par la Rédaction)

*Mots-clés:* ruffite, roselite, arsenate, structure cristalline, diffraction X, spectres Raman, Tierra Amarilla, Chili.

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## INTRODUCTION

A new member of the roselite group, ruffite, ideally  $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , has been found as a secondary mineral in the oxidation zone of the Cu–As orebody in the Maria Catalina mine, Pampa Larga mining district, Tierra Amarilla, Chile. The new mineral is named in honor of the RRUFF project, an Internet-based internally consistent and integrated database of Raman spectra, X-ray diffraction, and chemical data for minerals. The project currently has more than 3500 samples and 2000 mineral species in its database and provides a standard for mineralogists, geoscientists, materials scientists, and the general public for identification and characterization of minerals and inorganic materials. All data in the RRUFF project are freely accessible on the Internet (<http://ruff.info>). The RRUFF name is not an acronym, but rather it is the unique name chosen for the project by its principal financial supporter, Michael Scott, who was also the founding president of Apple Computers. Ruffite was discovered in the course of identifying minerals for the project, which involved the efforts of many people, including undergraduate and graduate students, post-doctoral research fellows, and project scientists. It was obtained as a donation by one of the authors, Robert Jenkins. The new mineral and its name have been approved by the Commission on New Minerals and Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2009–077). Part of the cotype sample has been deposited at the Mineral Museum of the University of Arizona (Catalogue # 18813) and the RRUFF project (deposition # R070431).

Minerals of the roselite group, which can be characterized with the general chemical formula  $X_2M(\text{TO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $X = \text{Ca}, \text{Na}$ ;  $M = \text{Mg}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Zn}$ , and  $T = \text{As}^{5+}, \text{S}^{6+}$ ), include the five members: roselite  $\text{Ca}_2\text{Co}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , brandtite  $\text{Ca}_2\text{Mn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , wendwilsonite  $\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , zincroselite  $\text{Ca}_2\text{Zn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , and kröhnkite  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ . They usually occur as minor or trace constituents in environments of hydrothermal alteration, and crystallize with monoclinic symmetry (space group  $P2_1/c$ ). The characteristic building unit of the roselite-type structure is an infinite chain of octahedra and tetrahedra with the composition  $[M(\text{TO}_4)(\text{H}_2\text{O})_2]$ , in which isolated  $\text{MO}_6$  octahedra are linked by corner-sharing with  $\text{TO}_4$  tetrahedra. This type of chain is commonly called the kröhnkite-type chain, as it was first observed in kröhnkite (Dahlman 1952, Hawthorne & Ferguson 1975). In addition, two other structurally distinct, triclinic mineral groups, namely the collinsite and fairfieldite groups, can also be described with the same general chemical formulae and kröhnkite-type chains as the roselite-type minerals (Fleck *et al.* 2002, Herwig & Hawthorne 2006). Recently, there has been a considerable amount of work on a variety of synthetic materials with the general composition  $X_2M(\text{TO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Fleck

*et al.* 2002, Fleck & Kolitsch 2003, Wildner & Stoilova 2003, Kolitsch 2006, Kolitsch & Fleck 2005, 2006). In particular, Fleck *et al.* (2002) proposed a classification scheme for all known compounds (over 50) with kröhnkite-type chains, dividing them into six different structural types labeled A to F on the basis of the structural symmetry and geometrical relations between the chains, as well as interstitial  $X$  cations. Thus far, minerals are known to adopt only structural types A, B, and D, which correspond to the collinsite, fairfieldite, and roselite groups, respectively. In this paper, we describe the physical and chemical properties of ruffite and its structural relationships with other members of the roselite group on the basis of the single-crystal X-ray diffraction and Raman spectroscopic data.

## DESCRIPTION

*Occurrence, physical and chemical properties, and Raman spectra*

Ruffite is a secondary mineral found in the oxidation zone of the Cu–As orebody in the Maria Catalina mine, Pampa Larga mining district, Tierra Amarilla, Chile (latitude  $22^\circ 3'$  S, longitude  $68^\circ 30'$  W). A detailed description of the geology and mineralogy of this area has been given by Parker *et al.* (1963). The Maria Catalina mine is located on the northeast side of the Pampa Larga wash at an altitude between 950 and 1000 meters. The history of the mine is unknown, but according to Parker *et al.* (1963), most of the production in the district took place between 1850 and 1910. The mine was inactive when they studied it in the early 1960s and is still inactive today. The vein in which ruffite was found is hosted in volcanoclastic rocks of the Lower Cretaceous Cerillos Formation near the southern contact of the dioritic Pampa Larga pluton; it strikes  $N10^\circ W$  and dips  $70\text{--}80^\circ W$  (Parker *et al.* 1963). This vein, which was mined for silver, ranges in thickness from 40 to 70 cm and can be traced for more than 300 meters on the surface. Primary mineralization is only found in the lowest parts of the mine, which consists of pyrite, stibnite, native arsenic, quartz, barite, and ankerite–siderite. The oxidized portion of the vein largely consists of barite and quartz with abundant mansfieldite. Silver is present as iodargyrite, chlorargyrite and native silver, as reported by Parker *et al.* (1963), but not observed on our sample. Other arsenates found at the property include alumopharmacosiderite, arsenolite, barahonite-(Al), betpakdalite, conichalcite, lavendulan, talmessite, phillipsbornite, and metazeunerite (Parker *et al.* 1963). Non-arsenate minerals include wulfenite, duftite and phosphohedyphane. Ruffite, on the cotype samples, is found closely associated with quartz, barite, mansfieldite, alumopharmacosiderite, conichalcite, metazeunerite, and barahonite-(Al).

Ruffite crystals are in granular or blocky aggregates and druses (single crystals up to  $0.30 \times 0.30 \times 0.30$

mm) (Fig. 1). It is pale to light blue and transparent with a white streak and vitreous luster. Ruffite is brittle, with a Mohs hardness of ~3.0; cleavage is perfect on {010}, and twinning is common on (100). The measured and calculated densities are 3.79(3) and 3.77(2) g/cm<sup>3</sup>, respectively. Ruffite is insoluble in water, acetone, and hydrochloric acid. Optically, it is biaxial (-), with  $\alpha$  1.725(1),  $\beta$  1.734(1),  $\gamma$  1.740(1),  $2V_{\text{meas}} = 80(2)^\circ$ ,  $2V_{\text{calc}} = 78^\circ$ ,  $Y = \mathbf{b}$ ,  $X \wedge c = 49^\circ$ ; it does not fluoresce under long- or short-wave ultraviolet light. The dispersion is weak, with  $r < v$ . The compatibility index [ $1 - (K_p/K_C)$ ] is 0.026 (excellent).

The chemical composition was determined with a CAMECA SX50 electron microprobe at 10 kV and 5 nA (Table 1). On the basis of the number of oxygen atoms bonded to As<sup>5+</sup>, which is 8 (see below), we obtain an empirical formula of Ca<sub>2.01</sub>Cu<sub>1.01</sub>(AsO<sub>4</sub>)<sub>2.02</sub>•1.9H<sub>2</sub>O, which can be simplified as Ca<sub>2</sub>Cu(AsO<sub>4</sub>)<sub>2</sub>•2H<sub>2</sub>O.

The Raman spectra of ruffite were collected on the randomly oriented crystal used for the single-crystal X-ray diffraction study (see below) on a Thermo Almega microRaman system, using a solid-state laser (100% power) with a wavelength of 532 nm and a thermoelectric cooled CCD detector. The laser is partially polarized, with 4 cm<sup>-1</sup> resolution and a spot size of 1  $\mu\text{m}$ .

#### X-ray crystallography

Both powder and single-crystal X-ray-diffraction data for ruffite were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK $\alpha$  radiation. The powder X-ray-diffraction data were processed using the Bruker program PILOT. Based on monoclinic symmetry (see below), the unit-cell parameters determined from the powder X-ray-diffraction data (Table 2) with the REFIN program (Bartelmehs *et al.* 1993) are a

5.892(5),  $b$  12.724(8),  $c$  5.722 (4) Å,  $\beta$  109.28(9)°, and  $V$  404.9(4) Å<sup>3</sup>.

Single-crystal X-ray-diffraction data for ruffite were collected from a nearly equidimensional crystal (0.05 × 0.05 × 0.60 mm) with frame widths of 0.5° in  $\omega$  and 30 s counting time per frame. All reflections were indexed on the basis of a monoclinic unit-cell (Table 3). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections indicate the unique space-group  $P2_1/c$  (#14). The crystal structure was solved and refined using SHELX97 (Sheldrick 2008). The positions of all atoms were refined with anisotropic displacement parameters, except for H atoms, which were refined with a fixed isotropic displacement parameter ( $U_{\text{eq}} = 0.04$ ). Final coordinates and displacement parameters of atoms are listed in Table 4, and selected bond-distances are listed in Table 5. A cif file and a table of structure factors are available from the Depository of Unpublished Data [document Ruffite CM49\_877].

## DISCUSSION

#### Crystal structure

Ruffite is isostructural with roselite (Hawthorne & Ferguson 1977). Its structure is characterized by isolated CuO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra that are linked by corner-sharing with AsO<sub>4</sub> tetrahedra to form the kröhnkite-type chains extending parallel to the  $c$  axis (Fig. 2). These chains are linked together by large Ca cations and hydrogen bonding. Herwig & Hawthorne (2006) presented a comprehensive analysis of the topology of hydrogen bonding for the roselite-group minerals, as well as the collinsite- and fairfieldite-group minerals. Our structural data on ruffite agree well with their analysis for the roselite-group minerals. It should be pointed out that the linkage between kröhnkite-type

TABLE 1. CHEMICAL COMPOSITION OF RRUFFITE

	1	2	3	4	5	6	7	8	9	Average
As <sub>2</sub> O <sub>5</sub> wt. %	50.83	50.21	50.40	50.62	50.66	49.63	50.47	49.93	50.60	50.37(39)
CaO	24.49	24.18	24.26	24.81	24.44	24.54	24.84	24.63	24.75	24.55(23)
CuO	17.78	17.58	17.28	17.56	17.48	17.21	17.16	17.37	17.80	17.47(23)
SO <sub>3</sub>	0.16	0.15	0.12	0.09	0.14	0.06	0.14	0.12	0.04	0.11(4)
Total	93.26	92.12	92.06	93.08	92.72	91.44	92.61	92.05	93.19	92.50(62)
H <sub>2</sub> O*	6.74	7.88	7.94	6.92	7.28	8.56	7.39	7.95	6.81	7.50(62)
Ca <i>apfu</i>	1.96	1.97	1.97	1.99	1.97	2.03	2.00	2.00	1.98	1.99(2)
Cu	1.00	1.02	0.97	0.99	0.99	0.99	0.97	0.99	1.00	0.99(2)
As	2.02	2.00	2.03	2.01	2.02	1.99	2.01	2.00	2.00	2.01(1)
Total	4.98	4.99	4.96	4.99	4.98	5.01	4.98	4.99	4.99	4.99(1)

\*: The amount of H<sub>2</sub>O was calculated by difference. Cation numbers are calculated on the basis of eight atoms of oxygen per formula unit (*apfu*).



FIG. 1. Photograph of pale or light blue ruffite crystals associated with green conichalcite and pale blue granular aggregates of barhonaite-(Al) on a matrix of white granular mansfieldite.

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

<i>l</i>	<i>d</i> <sub>meas</sub> (Å)	<i>h k l</i>	<i>l</i>	<i>d</i> <sub>meas</sub> (Å)	<i>h k l</i>
27	6.400(38)	0 2 0	15	1.830(3)	$\bar{1}$ 2 3
42	5.087(9)	1 1 0	17	1.793(1)	1 6 1
11	4.425(11)	$\bar{1}$ 1 1	25	1.732(1)	0 2 3
59	4.177(10)	1 2 0	15	1.701(2)	3 3 0
41	3.800(2)	$\bar{1}$ 2 1	16	1.659(2)	0 3 3
92	3.377(4)	1 3 0	37	1.595(4)	$\bar{3}$ 4 2
56	3.190(9)	0 4 0	11	1.564(2)	$\bar{3}$ 1 3
89	2.983(12)	1 2 1	18	1.537(2)	$\bar{2}$ 7 1
100	2.827(4)	$\bar{1}$ 0 2	10	1.524(4)	$\bar{1}$ 7 2
28	2.750(6)	$\bar{1}$ 1 2	19	1.483(2)	2 4 2
28	2.643(11)	$\bar{2}$ 2 1	17	1.430(1)	$\bar{4}$ 2 1
19	2.344(6)	$\bar{1}$ 3 2	19	1.383(3)	$\bar{1}$ 8 2
22	2.240(1)	$\bar{1}$ 5 1	12	1.376(1)	$\bar{2}$ 6 3
49	2.114(3)	$\bar{1}$ 4 2	9	1.340(1)	$\bar{2}$ 3 4
22	1.898(1)	$\bar{2}$ 4 2	8	1.269(1)	$\bar{2}$ 9 1
			16	1.193(3)	1 10 1

TABLE 3. SUMMARY OF CRYSTALLOGRAPHIC DATA STRUCTURE-REFINEMENT RESULTS FOR RUFFITE

Ideal structural formula	Ca <sub>2</sub> Cu(AsO <sub>4</sub> ) <sub>2</sub> •2H <sub>2</sub> O
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
Unit-cell parameters	
<i>a</i> , <i>b</i> (Å)	5.8618(2), 12.7854(5)
<i>c</i> (Å), β (°)	5.7025(2), 109.425(2)
<i>V</i> (Å <sup>3</sup> )	403.05(3)
<i>Z</i>	2
ρ <sub>calc</sub> (g/cm <sup>3</sup> )	3.77
λ (Å)	0.71069
μ (mm <sup>-1</sup> )	12.17
θ range for data collection (°)	3.19 to 34.31
No. of reflections collected	5736
No. of independent reflections	1658
No. of reflections with <i>I</i> > 2σ( <i>I</i> )	1435
No. of parameters refined	77
R(int)	0.023
Final R factors [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> = 0.023, wR <sub>2</sub> = 0.060
Final R factors (all data)	R <sub>1</sub> = 0.030, wR <sub>2</sub> = 0.062
Goodness-of-fit	1.42

chains in minerals and synthetic compounds with the composition  $X_2M(TO_4)_2 \cdot 2H_2O$  has been a subject of extensive investigations because of its importance in understanding structural hierarchies or classifications of these materials and their relative fields of stability (Hawthorne & Ferguson 1977, Fleck *et al.* 2002, Fleck & Kolitsch 2003, Wildner & Stoilova 2003, Keller *et al.* 2004, Kolitsch & Fleck 2005, 2006, Herwig & Hawthorne 2006).

As in other roselite-type minerals, the Ca cations in ruffite are coordinated by seven anions at distances

between 2.376 and 2.493 Å, with an average distance of 2.429 Å (Table 5). An examination of the reported structural data reveals that all  $MO_4(H_2O)_2$  octahedra in the roselite-group minerals are relatively distorted, with four short and two long bonds. However, owing to the strong Jahn–Teller effect, the  $CuO_4(H_2O)_2$  octahedron in ruffite is the most distorted of all measured to date in terms of the octahedron quadratic elongation (OQE) (Robinson *et al.* 1971). This value is 1.0294 for ruffite and 1.0082–1.0276 for other roselite-group minerals, including kröhnkite, which also contains the

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN RRUFFITE

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Ca	0.56418(9)	0.12303(4)	0.21155(9)	0.0089(2)	0.0094(2)	0.0119(2)	-0.0010(2)	0.0038(2)	-0.0003(2)	0.0100(1)
Cu	0	0	0	0.0109(2)	0.0121(2)	0.0136(2)	-0.0044(2)	0.0016(2)	0.0001(2)	0.0128(1)
As	0.22626(4)	0.12128(2)	0.54652(4)	0.0074(1)	0.0076(1)	0.0084(1)	-0.0001(1)	0.0019(1)	0.0002(1)	0.0080(1)
O1	0.2381(3)	0.0379(1)	0.3183(3)	0.0102(8)	0.0135(8)	0.0118(8)	-0.0048(6)	0.0032(6)	-0.0006(6)	0.0119(3)
O2	0.3018(3)	0.0542(1)	0.8149(3)	0.0124(8)	0.0104(7)	0.0106(8)	0.0026(6)	0.0037(6)	0.0011(6)	0.0112(3)
O3	0.9533(3)	0.1749(1)	0.4816(4)	0.0083(7)	0.0126(7)	0.0142(8)	0.0001(6)	0.0020(7)	0.0041(6)	0.0121(3)
O4	0.4468(3)	0.2067(1)	0.5496(4)	0.0114(8)	0.0116(7)	0.0156(9)	-0.0024(7)	0.0056(7)	-0.0049(6)	0.0126(4)
O5	0.8261(4)	0.1361(1)	0.9559(4)	0.0112(8)	0.0095(7)	0.0105(8)	-0.0011(6)	0.0004(6)	-0.0009(6)	0.0112(3)
H1	0.731(7)	0.141(3)	0.855(9)							0.04
H2	0.897(7)	0.197(3)	0.983(8)							0.04

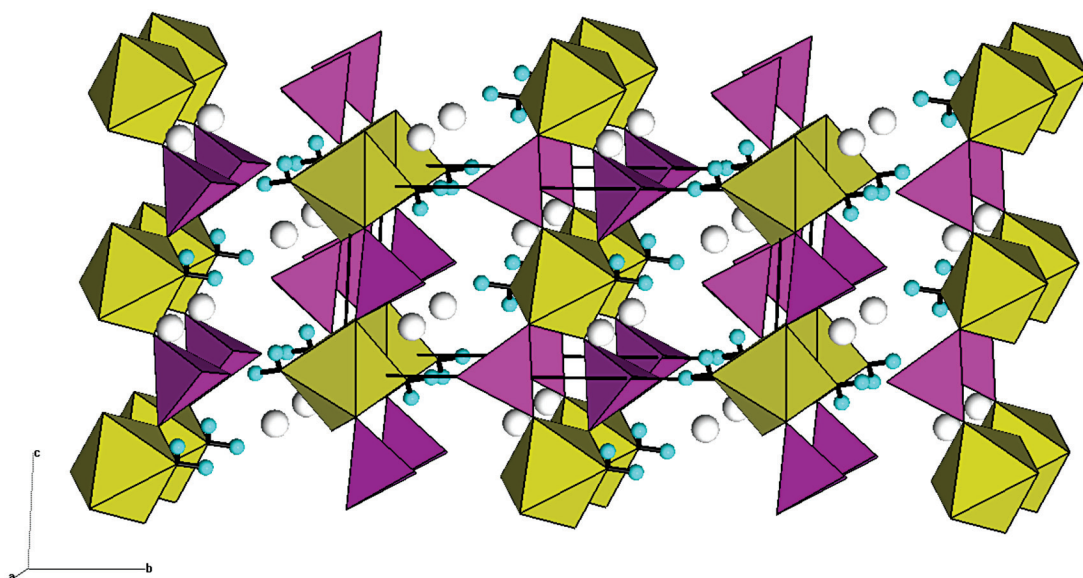


FIG. 2. Crystal structure of ruffite. Yellow octahedra:  $\text{CuO}_4(\text{OH})_2$ , purple tetrahedra:  $\text{AsO}_4$ , white spheres: Ca cations, and light blue spheres: H atoms.

$\text{CuO}_4(\text{H}_2\text{O})_2$  octahedra. Interestingly, the  $\text{AsO}_4$  tetrahedron in ruffite is also the most distorted among all roselite-type minerals, as measured by the tetrahedron quadratic elongation (TQE). In fact, there appears to be a positive correlation between the OQE and TQE values for the roselite-group minerals. This correlation may be understood from the linkage between the  $\text{AsO}_4$  tetrahedra and  $\text{MO}_4(\text{H}_2\text{O})_2$  octahedra. In the roselite-type structure, each  $\text{AsO}_4$  tetrahedron shares two corners (O2 and O3) with adjacent  $\text{MO}_4(\text{H}_2\text{O})_2$  octahedra, *i.e.*,  $\text{As-O2-M}$  and  $\text{As-O3-M}$ . [Note that the labeling of O atoms in ruffite follows that for roselite (Hawthorne & Ferguson 1977) and wendwilsonite (Kolitsch & Fleck

TABLE 5. SELECTED NON-HYDROGEN BOND DISTANCES (Å) IN RRUFFITE

Ca --O1	2.446(2)	Cu --O1 ×2	1.948(2)	As --O1	1.701(2)
--O2	2.419(2)	--O2 ×2	2.443(2)	--O2	1.680(2)
--O3	2.438(2)	--O5 ×2	1.990(2)	--O3	1.666(2)
--O3	2.383(2)			--O4	1.688(2)
--O4	2.376(2)	<Cu-O>	2.127		
--O4	2.493(2)			<As-O>	1.684
--O5	2.449(2)				
<Ca-O>	2.429				



2006), but differs from that for brandtite (Herwig & Hawthorne 2006) and zincroselite (Keller *et al.* 2004)]. Within an  $MO_4(H_2O)_2$  octahedron, the  $M-O2$  bond is invariably the longest, whereas the  $M-O3$  bond is one of the short ones. The increased OQE value means that there is a greater difference between the  $M-O2$  and  $M-O3$  (as well as  $O5$ ) bond lengths. To maintain the appropriate bond-valence sums for  $O2$  and  $O3$ , the difference between the  $As-O2$  and  $As-O3$  bond distances will have to be augmented correspondingly, thus giving rise to the increased TQE value for the  $AsO_4$  tetrahedron.

### Raman spectra

There have been numerous studies on a variety of arsenate compounds, including roselite, talmessite, and "talmessite-Co", by means of infrared and Raman spectroscopic techniques (Frost 2009, Frost *et al.* 2009, 2010, and references therein). Here, we present our Raman spectroscopic measurements of ruffite in Figure 3, along with the Raman spectra of other arsenate minerals in the roselite group from the RRUFF project for comparison, including roselite,

zincroselite, brandtite, and wendwilsonite (deposition # R100191, R100192, R070170, and R100175, respectively). Based on previous studies on roselite and other related arsenates (Frost 2009, Frost *et al.* 2009), we made a tentative assignment of observed Raman modes for ruffite (Table 6). It is obvious from Figure 3 that the wavenumber of the symmetric stretching ( $\nu_1$ ) mode of the  $AsO_4$  group for brandtite (at  $\sim 822\text{ cm}^{-1}$ ) is smaller than that for ruffite by  $\sim 17\text{ cm}^{-1}$ . Because both our ruffite and brandtite are nearly pure end-members, this shift in wavenumber may be ascribed to the substitution of Mn for Cu. Similar results have also been observed for the libethenite group of minerals between olivenite,  $Cu_2AsO_4(OH)$ , and eveite,  $Mn_2AsO_4(OH)$  (see the RRUFF database at <http://rruff.info/olivenite> and <http://rruff.info/eveite>). Note that the  $\nu_1$  mode of the  $AsO_4$  group for roselite, zincroselite, and wendwilsonite are all split. Given the chemical compositions determined for these three minerals [ $Ca_{1.99}(Co_{0.77}Mg_{0.18}Mn_{0.03})(AsO_4)_2 \cdot 2H_2O$  for roselite,  $Ca_{2.06}(Zn_{0.90}Mn_{0.06}Mg_{0.05}Fe_{0.01})(As_{0.99}O_4)_2 \cdot 2H_2O$  for zincroselite, and  $Ca_{2.01}(Mg_{0.61}Co_{0.27}Zn_{0.07}Mn_{0.05})(AsO_4)_2 \cdot 2H_2O$  for wendwilsonite], we may relate such splitting to the presence of mixed cations (Mg, Co, Mn,

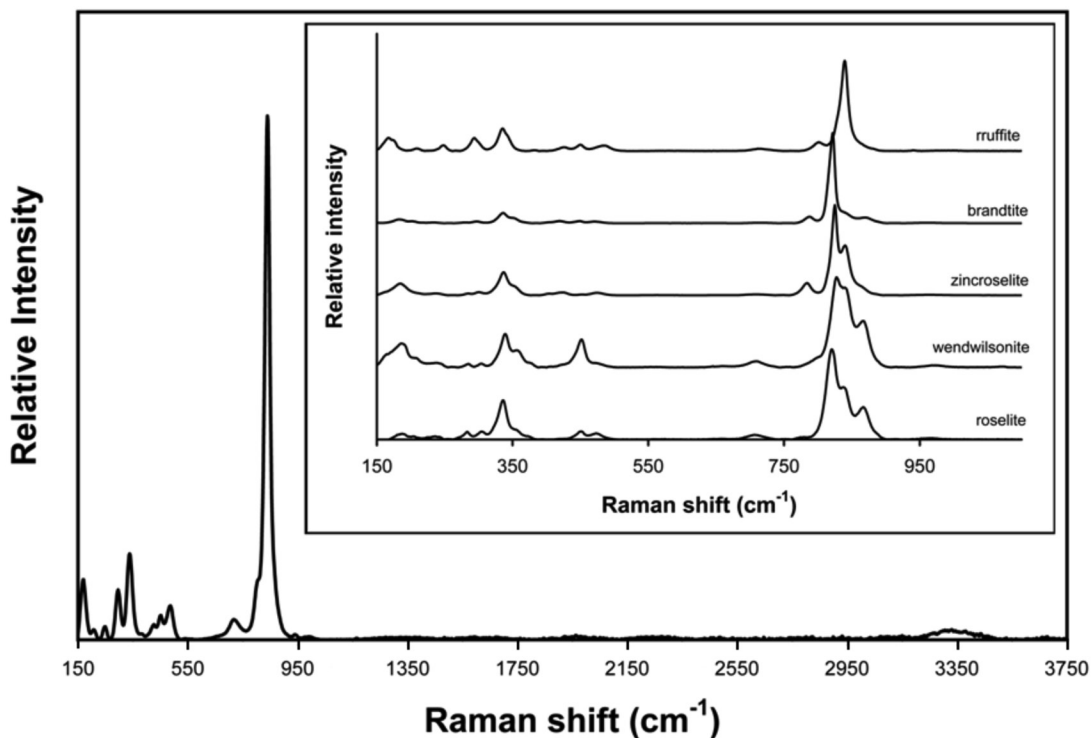


FIG. 3. Raman spectra of ruffite, along with those (between 150 and  $1100\text{ cm}^{-1}$ ) of roselite, zincroselite, brandtite, and wendwilsonite from the RRUFF project (see the text for details) for comparison. The spectra of the inset figure are shown with a vertical offset for more clarity.

TABLE 6. TENTATIVE ASSIGNMENT OF RAMAN BANDS FOR RRUFFITE

Bands (cm <sup>-1</sup> )	Intensity	Assignment
3335, 3147	Weak, broad bands	H <sub>2</sub> O ν <sub>1</sub> - ν <sub>3</sub> symmetric and anti-symmetric stretching
866, 803, 715	Weak bands	ν <sub>3</sub> (AsO <sub>4</sub> ) anti-symmetric stretching
839	Very strong, sharp	ν <sub>1</sub> (AsO <sub>4</sub> ) symmetric stretching
715	Weak	H <sub>2</sub> O librational mode
485, 451, 426	Relatively strong, sharp	ν <sub>4</sub> (AsO <sub>4</sub> ) anti-symmetric bending
335, 294	Strong, sharp	ν <sub>2</sub> (AsO <sub>4</sub> ) symmetric bending
260–150	Relatively strong, sharp	Lattice vibrational modes and Cu–O and Ca–O interactions

Zn, and Fe) at the *M* site. Moreover, it is worth noting that our Raman spectrum of roselite, which, as our ruffite, was also measured from the same crystal examined by single-crystal X-ray diffraction and electron-microprobe analysis, appears to be different from that documented by Frost (2009), despite the fact that the roselite sample used by Frost (2009) is from the same locality (Bou Azzer, Morocco). Specifically, between 750 and 900 cm<sup>-1</sup>, Frost *et al.* (2009) observed only two bands, a relatively intense one at 798 cm<sup>-1</sup> and a weak one at 864 cm<sup>-1</sup>. In contrast, there exist four obvious bands in the same region for our roselite, namely, a very intense one at ~821 cm<sup>-1</sup>, two relatively weak ones at 840 and 868 cm<sup>-1</sup>, and a very weak one at 780 cm<sup>-1</sup>. It is unclear why the ν<sub>1</sub> mode, which should be the most intense band between 820 and 845 cm<sup>-1</sup> for the roselite-type arsenates, was not detected by Frost *et al.* (2009).

Remarkably, every arsenate mineral of the roselite group (*P*2<sub>1</sub>/*c* symmetry) has a polymorph in the collinsite group (*P*1̄ symmetry), namely, roselite – beta-roselite, brandtite – parabrandsite, wendwilsonite – talmessite, and zincroselite – gaitite. They are found in close proximity to each other. Thus, the discovery of ruffite begs the question whether ruffite, like other arsenate minerals of the roselite group, undergoes a polymorphic transformation to a collinsite-type structure. At present, no convincing evidence has been established regarding the relative stability of the corresponding arsenate polymorphs between the roselite and collinsite groups. Nevertheless, Keller *et al.* (2004) noted that the activity of Zn<sup>2+</sup> and the redox potential with respect to the [AsO<sub>3</sub>]<sup>3-</sup> – [AsO<sub>4</sub>]<sup>3-</sup> couple were evidently higher for the mineral association of zincroselite than for those of gaitite. Further research on ruffite may shed light on its possible polymorphism and the relative fields of stability of the polymorphs between the roselite and collinsite groups.

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