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Ajoite: new data

GEORGE Y. CHAO

Department of Geology, Carleton University
Ottawa, Ontario K1S 5B6, Canada

Abstract

New data show that ajoite is triclinic, $P1$ or $P\bar{1}$, $a = 13.637$, $b = 14.507$, $c = 13.620$Å, $\alpha = 107.16$, $\beta = 105.45$, $\gamma = 110.57°$; $Z = 3$. The mineral is biaxial positive, $2V = 80°$, $\alpha = 1.550$, $\beta = 1.583$, $\gamma = 1.641$ (in Na light); pleochroic: X = very light bluish green, $Y \sim Z$ = brilliant bluish green. {010} cleavage is perfect. The orientation of the principal vibration directions is defined by the spherical coordinates X(26.5°, 80°), $\bar{Y}$(118°, 79°), Z(−104.5°, 15°). The extinction angle $c:Z'$ on (010) is 15°. Electron microprobe and chemical analyses gave SiO_2 41.2, Al_2O_3 3.81, CuO 42.2, MnO 0.02, FeO 0.11, CaO 0.04, Na_2O 0.84, K_2O 2.50, H_2O (TGA to 1000°C) 8.35, sum 99.07 wt.%. The analysis corresponds to $(K_{0.70}Na_{0.36}Ca_{0.01})(Cu_{6.97}Fe_{0.02})Al_{0.98}Si_{9.00}O_{24}(OH)_6 \cdot 3.09H_2O$ or ideally, $(K,Na)Cu_7AlSi_9O_{24}(OH)_6 \cdot 3H_2O$. TGA showed a two-stage dehydration; 50% of the total water was released between 70° and 425°C and the rest between 425° and 800°C. Half of the water is zeolitic in nature.

Introduction

Ajoite, first described by Schaller and Vlisidis (1958) from Ajo, Pima County, Arizona, was thought to be monoclinic on the basis of optical studies. The chemical formula was given as $Al_2O_3 \cdot 6CuO \cdot 10SiO_2 \cdot 5\frac{1}{2}H_2O$. The published X-ray powder diffraction data, however, indicated a significant amount of quartz in the analyzed material, the 3.34Å reflection of quartz being the second strongest in the powder pattern with a relative intensity of 25 on a scale of 100. Thus the reported analysis and the proposed formula are likely to be erroneous. A restudy of this unusual mineral was therefore deemed worthwhile.

The material came from the New Cornelia Mine, Ajo, Pima County, Arizona, purchased in 1965 from the Southwest Scientific Company, Scottsdale, Arizona. The bluish green ajoite occurs in veinlets and as sprays of fine, prismatic, bladed crystals lining irregular shaped vugs in monzonite stained in places by a mixture of hematite and sericite. Calcite crystals are common in the vugs and minor amounts of barite are noted. Shattuckite and conichalcite, reported to be associated with the type ajoite material, are characteristically absent. The ajoite crystals (Fig. 1), average 0.01 × 0.1 × 0.4 mm, are elongated along c and flattened on (010). {010} is the most prominent form and {100} and {1$\bar{1}$0} are much less prominent but are always present. The termination on c may be either {001} or {$\bar{2}$03} or both.

X-ray crystallography

Weissenberg and precession photographs show the mineral to be triclinic, $P1$ or $P\bar{1}$. The parameters of the reduced cell obtained from these photographs and refined by a least-squares method using Gandolfi diffraction data (Table 1) are $a = 13.637(5)$, $b = 14.507(4)$, $c = 13.620(2)$Å, $\alpha = 107.16(2)$, $\beta = 105.45(2)$, $\gamma = 110.57(2)°$. The single-crystal photographs display strong pseudo-periods along a and c as reflections with h not equal to 4n and $h + l$ not equal to 5n are either very weak or absent. This is also evident in the indexed powder diffraction data (Table 1) in which most reflections are of the type with h = 4n and $h + l$ = 5n.

The conventional Debye-Scherrer powder diffraction photographs show a strong preferred orientation effect on the $0k0$ reflections, suggesting that ajoite possesses a perfect {010} cleavage. The Debye-Scherrer photographs also show that the d values of some diffraction lines, particularly 4$\bar{2}$1, 4$\bar{1}$1 and the $0k0$ family of lines, tend to vary, presumably due to structural damage induced by grinding. Comparisons of the present data with the data from Schaller and Vlisidis (1958) reveal many extra lines in the latter, apparently due to quartz and sericite.

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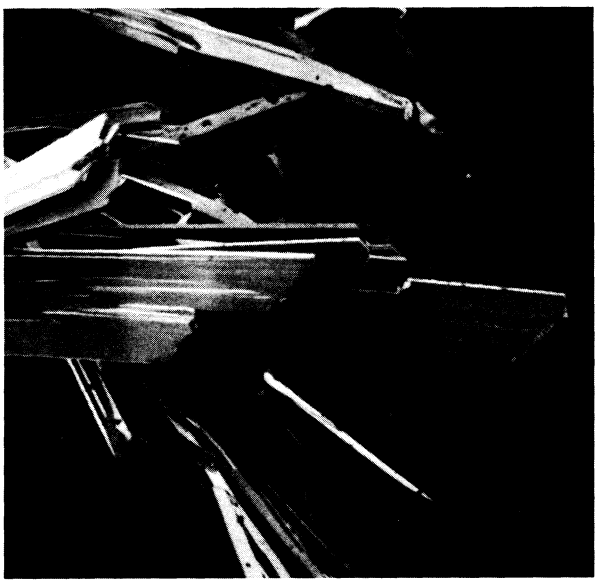

Fig. 1. Scanning electron microscope photomicrograph of ajoite showing the bladed habit. The width of the large crystal is about 0.1 mm.

Optical properties

The optical properties of ajoite were determined in sodium light at room temperature on a spindle stage. All refractive index liquids used were checked with an Abbé refractometer. Crystals previously oriented by X-ray goniometry were re-oriented optically using extinctions and interference figures. The errors in the orientation of the indicatrix were estimated to be less than 2°. 2V was measured by direct observation of the optic axes on crystals oriented to rotate about the optic normal.

In white light the mineral is distinctly pleochroic with X = very light bluish green (ISCC-NBS color designation 162), $Y \sim Z$ = brilliant bluish green (ISCC-NBS color designation 159). Dispersion is indiscernible. The optical data of ajoite are compared with the data from Schaller and Vlisidis in Table 2. The orientation of the principal vibration directions with respect to the crystallographic directions is shown in Figure 2 and is defined by the spherical coordinates: X(26.5°, 80°), $\overline{Y}$(118°, 79°), Z(−104.5°, 15°). The extinction angle $c \wedge Z'$ on (010) is 15°, confirming the value determined by Berman (Schaller and Vlisidis, 1958).

Table 1. X-ray powder-diffraction data of ajoite

hkl	d(calc.)	d(obs.)	I/Io	hkl	d(calc.)	d(obs.)	I/Io
010	12.258	12.25	100	$44\bar{4}$	2.073	2.072	2
020	6.129	6.12	5	$06\bar{5}$	2.042	2.040	3
$1\bar{1}2$	5.259	5.24	2	421	2.039		
$12\bar{1}$	5.242			$44\bar{4}$	1.989	1.989	4
$11\bar{3}$	4.522	4.52	3	025	1.946	1.946	2
030	4.086	4.08	10	$45\bar{4}$	1.856	1.858	2
$33\bar{1}$	3.666	3.666	1	$07\bar{5}$	1.836	1.834	2
130	3.391	3.381	8	$83\bar{3}$	1.691	1.692	2
$1\bar{4}0$	3.377			$46\bar{4}$	1.665	1.664	2
040	3.065	3.061	10	$84\bar{3}$	1.663		
$42\bar{1}$	2.989	2.983	3	$85\bar{3}$	1.608	1.607	2
$41\bar{1}$	2.839	2.832	8	$46\bar{6}$	1.606		
$41\bar{4}$	2.668	2.669	4	$47\bar{6}$	1.557	1.558	2
$03\bar{5}$	2.590	2.587	3	$86\bar{3}$	1.533	1.533	1
401	2.586			080	1.532		
$42\bar{4}$	2.516	2.518	6	$09\bar{5}$	1.490	1.490	2
$04\bar{5}$	2.455	2.455	12	$42\bar{9}$	1.488		
005	2.370	2.369	2	$43\bar{9}$	1.478	1.477	4
$41\bar{1}$	2.304	2.302	6	$41\bar{9}$	1.477		
$43\bar{4}$	2.302					1.311	2
$05\bar{5}$	2.257	2.258	8			1.298	2
$46\bar{1}$	2.257					1.270	2
$43\bar{4}$	2.216	2.214	3			1.246	2
015	2.160	2.158	4				

Data obtained with a 114.6 mm Gandolfi camera, using uncrushed crystals, CuKα radiation and NBS silicon as an internal standard. Intensities were estimated visually.

Table 2. Optical properties of ajoite

	Present Study*	Schaller & Vlisidis
α	1.550(1)	1.565
β	1.583(1)	1.590
γ	1.641(1)	1.650
$2V_Z$ meas.	80(1)°	---
calc.	76.4°	68°

**All measurements are for sodium light at 24°C.*

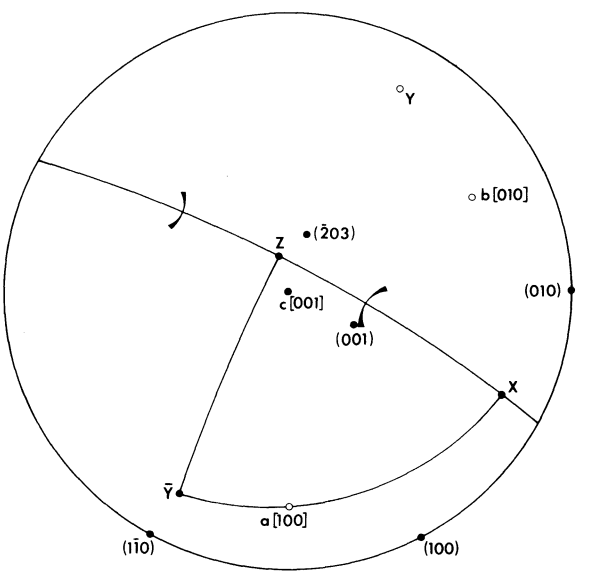

Fig. 2. Stereographic projection of optical and crystallographic elements of ajoite.

Table 3. Chemical analysis of ajoite

	Wt. percent	Number of cations
SiO_2	41.2	9.00
Al_2O_3	3.81	0.98
CuO	42.2	6.97
MnO	0.02	0.004
FeO	0.11	0.02
CaO	0.04	0.01
Na_2O	0.84	0.36
K_2O	2.50	0.70
H_2O	8.35	12.17
Total	99.07	

SiO_2, Al_2O_3, CuO by electron microprobe using fluorphlogopite(Si, Al) and covellite(Cu) as standards (Analyst: Paul R. Mainwaring). Other constituents by conventional wet analysis (Analyst: D. Mah). H_2O by TGA to 1100°C. Number of cations were calculated on the basis of 27 oxygen atoms not including H_2O.

Chemical composition

Because of the strong cratering effect on the mineral under the electron beam only the major constituents (Cu, Si, and Al) were analyzed using the electron microprobe. For Na, K, and other minor constituents the electron microprobe analyses gave poor reproducibility. These elements were therefore analyzed by conventional methods on hand-picked material, CaO by titration with EDTA, FeO by titration with $K_2Cr_2O_7$, Na_2O and K_2O by flame photometry, and MnO by spectrophotometry. Water was determined by TGA to 1000°C. The results are given in Table 3. The analysis may be recalculated, on the basis of 27 oxygen atoms per formula, to $(K_{0.70}Na_{0.36}Ca_{0.01})\ (Cu_{6.97}Fe_{0.02})\ Al_{0.98}Si_{9.00}O_{27} \cdot 6.09H_2O$, or ideally, $(K,Na)Cu_7AlSi_9O_{27} \cdot 6H_2O$. Assuming Z to be 3, the calculated density is 2.951g/cm^3, in good agreement with the observed density of 2.96g/cm^3 reported by Schaller and Vlisidis.

Thermal study

TGA curves of ajoite showed a two-stage dehydration (weight loss). Half of the water was released between 70° and 425°C and the rest between 425° and 800°C. The dehydrated material quenched from 1000°C was black and was found to be tenorite (CuO) by X-ray diffraction. No crystalline silicate phase was detected. When quenched from 425°C, after completion of the first stage of dehydration, the mineral regained nearly all of the lost water within 15 minutes. The rehydrated material turned green but gave an X-ray diffraction pattern identical to that of the unheated ajoite. Thus one half of the water present in ajoite is zeolitic in nature and the other half, released between 425° and 800°C, is most likely present as OH. The most probable formula for ajoite is, therefore, $(K,Na)Cu_7AlSi_9O_{24}(OH)_6 \cdot 3H_2O$.

Acknowledgments

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References

Schaller, W. T. and Vlisidis, A. C. (1958) Ajoite, a new hydrous aluminum copper silicate. American Mineralogist, 43, 1107–1111.

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