

BARICITE, THE MAGNESIUM ANALOGUE OF VIVIANITE, FROM YUKON TERRITORY, CANADA

B. D. STURMAN AND J. A. MANDARINO

Dept. of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park,
Toronto, Ontario, M5S 2C6

ABSTRACT

Baricite occurs as plates parallel to {010} up to 12 cm in maximum dimension and up to 5 cm thick in fractures in a sideritic iron formation in the northeastern part of Yukon Territory. Baricite is colorless to pale blue and has a white streak which changes to blue after several days. The lustre is vitreous and is pearly on fresh {010} surfaces. There is one perfect cleavage {010}; thin cleavage flakes are flexible. Hardness is $1\frac{1}{2}$ to 2; D (meas.) is 2.42 g/cm³, D (calc.) is 2.448 g/cm³. Baricite is biaxial (+), n_{α} 1.554(1), n_{β} 1.564(1), n_{γ} 1.595(1) (Na), $2V$ 59°(2) (meas.) and 60° (calc.). Dispersion, $r < v$ is weak. $X = b$ and $Z \perp c$ is +32°(1). The mineral is monoclinic, space group $C2/m$, a 10.075(4), b 13.416(8), c 4.670(4) Å, β 104° 52' (2), $a:b:c = 0.7510:1.0:3.481$, $V = 610.1$ (4) Å³, $Z = 2$. The strongest lines in the X-ray powder diffraction pattern are: 6.71(100) (020), 3.196(40) (131), 2.956(60) (311,201), 2.699(70) (221,041), 2.526(50) (241), and 2.418(35) (401) all in Å for Fe/Mn radiation. The ideal chemical formula of baricite is $(Mg_{1.64}Fe^{+2}_{1.21}Fe^{+3}_{0.15})(PO_4)_2(OH)_{0.15} \cdot 7.85H_2O$. TGA gives a simple one-stage weight loss curve. An endothermic peak occurs at 220°C and an exothermic peak occurs at 705°C. The mineral is named in honor of Prof. Dr. Ljudevit Baric of the University of Zagreb.

SOMMAIRE

La baricite que l'on trouve dans les fissures d'une formation de fer sidéritique située dans le Nord-Est du Territoire du Yukon se présente sous forme de plaquettes {010}, dont la longueur peut atteindre 12 cm et l'épaissir, 5 cm. Incolore ou d'un bleu pâle, elle possède une rayure blanche qui vire au bleu après plusieurs jours. Son éclat est d'ordinaire vitreux, mais nacré sur les faces fraîches du clivage parfait {010}. Les paillettes minces de clivage sont flexibles. La dureté est égale à $1\frac{1}{2}$ ou 2; D (mes.) = 2.42, D (calc.) = 2.448. La baricite est biaxe positive. n_{α} 1.554(1), n_{β} 1.564(1), n_{γ} 1.595(1) (Na), $2V$ 59°(2) (mes.) et 60° (calc.). La dispersion $r < v$ est faible, $X = b$ et $Z \perp c$ est +32°(1). Le minéral est monoclinique, de groupe spatial $C2/m$; a 10.075(4), b 13.416(8), c 4.670(4) Å, β 104° 52' (2)', $a:b:c = 0.7510:1.0:3.481$, $V = 610.1$ (4) Å³, $Z = 2$. Les raies les plus intenses du diagramme de poudre correspondent aux espacements suivants (en Å): 6.71(100) (020), 3.196(40) (131),

2.956(60) (311,201), 2.699(70) (221,041), 2.526(50) (241), et 2.418(35) (401), en rayonnement Fe/Mn. La formule chimique idéalisée de la baricite est. $(Mg_{1.64}Fe^{+2}_{1.21}Fe^{+3}_{0.15})(PO_4)_2(OH)_{0.15} \cdot 7.85H_2O$. L'analyse thermogravimétrique donne une courbe simple pour la perte de poids en un seul échelon. Le pic endothermique se trouve à 220°C et le pic exothermique à 705°C. Le nom du minéral honore le Professeur Dr Ljudevit Baric de l'Université de Zagreb.

(Traduit par la Rédaction)

INTRODUCTION

Baricite occurs as large plates parallel to {010} which are up to 12 cm in maximum dimension and up to 5 cm thick. It is found in fractures in a sideritic iron formation in the Big Fish River-Blow River area in the northeastern part of Yukon Territory. Quartz, siderite, vivianite, and lazulite are minerals directly associated with baricite, although many other phosphate minerals are found in the vicinity. The locality is described briefly by Mandarino & Sturman (1976) in their paper on kulanite, another new species from the same deposit. Baricite, as a mineral and a mineral name, has been approved by the Commission on New Minerals and Mineral Names, I. M. A.

PHYSICAL PROPERTIES

Baricite is colorless to pale blue, the intensity of the blue color depending on the amount of oxidation of the iron. The streak is white to pale blue, but the color of the powder changes to dark blue after several days. The lustre is vitreous and is pearly on fresh surfaces parallel to {010}. Cleavage {010} is perfect and thin cleavage flakes are flexible. The hardness is $1\frac{1}{2}$ to 2. The density measured with the Berman microbalance is 2.42 g/cm³. The mineral does not fluoresce in ultraviolet light.

OPTICAL DATA

Baricite is optically biaxial (+). The obtuse bisectrix X is perpendicular to the cleavage {010} and neither optic axis can be seen on

the universal stage when a cleavage flake is used as a section. Therefore, $2V$ was determined on tilted grains in a grain mount and the accuracy of the determination was lower than normal because of the tendency of the flakes to bend. In Table 1, the optical data for baricite are compared to the optical data for vivianite given by Baric (1965).

TABLE 1. OPTICAL DATA FOR BARIĆITE AND VIVIANITE

	Barićite Yukon Territory, Canada This study	Vivianite Starl Trg, Yugoslavia Barić (1965)
n_a	1.554(1)	1.5857
n_b	1.564(1)	1.6027
n_c	1.595(1)	1.6354
$2V_s$ (meas.)	$55^\circ \pm 2^\circ$	$73^\circ 21'$
$2V_s$ (calc.)	$60^\circ 09'$	$72^\circ 51'$
dispersion orientation	$x < v$, weak $X = b$	$x < v$, weak $X = b$
pleochroism	$Z_A\sigma = +32^\circ \pm 1^\circ$ nil	$Z_A\sigma = 28^\circ 06'$ nil

Because of the absence of any crystal or cleavage faces other than {010}, the position of the c -axis had to be determined by means of single-crystal X-ray diffraction methods. The $Z_A\sigma$ angle of $+32^\circ$ was measured on a cleavage flake in which the position of the c -axis had been located by the precession method.

Under the microscope, cleavage flakes of baricite are colorless or pale blue. The blue color is seen mainly at the edges or other parts of the cleavage flakes where mechanical distortion has taken place by bending, scratching, or cutting. This change from colorless to blue indicates oxidation of the iron. Blue grains are pleochroic with X blue, Y and Z colorless.

Slight variations in refractive indices were observed in several plates of baricite. These may be due, in part, to different $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratios. Because the same variations exist in colorless material, it is more probable that they are caused by variations in the Mg:Fe ratio. For the chemical analysis, special care was taken to choose only material with the lowest refractive indices as such material has the highest Mg content.

CRYSTALLOGRAPHY

Baricite is developed as plates parallel to {010}. No other forms were observed and the directions of the a and c crystallographic axes could be determined only by X-ray diffraction methods. Table 2 compares the unit cell data for baricite determined by the precession method, the unit-cell data for baricite calculated from the X-ray powder diffraction data using 15 d -values and the program of Evans *et al.* (1963), and the unit-cell data for vivianite given by Mori & Ito (1950).

TABLE 2. UNIT CELL PARAMETERS OF BARIĆITE AND VIVIANITE

Space group	Baricite		Vivianite
	This study	From powder data	Mori & Ito (1950)
$C2/m$	$C2/m$	$C2/m$	$C2/m$
a	10.08 Å	10.075(4) Å	10.08 Å
b	13.42	13.416(8)	13.43
c	4.68	4.670(4)	4.70
β	$104^\circ 50'$	$104^\circ 52'$	$104^\circ 30'$
$a:b:c$	0.7511:1:0.3487	0.7510:1:0.3481	0.75061:1:0.3500
volume (Å ³)	612.0	610.1	616.0
z	2	2	2

The X-ray powder diffraction patterns of baricite and vivianite are very similar. The powder data for baricite, given in Table 3, were obtained from a pattern prepared in a Debye-

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR BARIĆITE

I	d_{obs}	d_{calc}	hkl	I	d_{obs}
25	7.9	7.88	110	5	1.886
100	6.71	6.71	020	1	1.878
20	4.87	4.87	200	10	1.768
5	4.51	4.51	001	30	1.676
15	4.33	4.32	111	10	1.667
10	4.07	4.06	130	15	1.648
20	3.832	3.837	201	10	1.593
5	3.610	3.607	111	25	1.576
1	3.341	3.330	221	5	1.539
40	3.196	3.195	131	5	1.514
60	2.956	2.955	201	1	1.494
70	2.699	2.692	311	15	1.477
10	2.626	2.627	221	10	1.459
50	2.526	2.525	241	5	1.431
35	2.418	2.417	401	1	1.236
15	2.311	2.313	151	2	1.179
5	2.275	2.274	421	2	1.168
30	2.217	2.217	241	1	1.143
10	2.179	2.181	151	5	1.123
20	2.066			5	1.109
5	2.001			10	1.034
5	1.959			5	1.008
10	1.922			5	0.994

Fe/Mn radiation; 114.6 mm diameter camera.

Scherrer camera of 114.6 mm diameter using Mn-filtered Fe-radiation. Intensities were estimated visually. There are no visible differences in d -values or in intensities between a pattern made from freshly ground baricite and a pattern made from baricite powder ground two weeks earlier.

THERMAL DATA

Simultaneous DTA-TGA runs were made in a Mettler Thermalanalyzer in oxygen and nitrogen atmospheres. Alumina was used as the reference substance, the heating rate was $8^\circ\text{C}/\text{minute}$, and the temperature range was 25° – 850°C .

A sample weighing 210.4 mg underwent a weight loss of 29.23% in an oxygen atmosphere. In a nitrogen atmosphere a weight loss of 28.96% resulted from a sample weighing 194.4 mg. The two percentage weight losses are very close because the samples had undergone al-

most complete oxidation during grinding. In both runs, the TGA curve is a simple one-stage weight loss curve.

The DTA curves of both samples show an endothermic peak at 220°C and an exothermic peak at 705°C.

CHEMICAL COMPOSITION

It was planned to subject the material selected for chemical analysis to two thermogravimetric analyses — one in an oxygen atmosphere and one in a nitrogen atmosphere. The residue from the oxygen TGA would then have been analyzed for MgO, Fe₂O₃, and P₂O₅. The two weight losses from the TGA runs together with the data from the chemical analysis would have provided data which would enable the amounts of H₂O, FeO, and Fe₂O₃ to be determined. This method was used by Mandarino & Sturman (1976) in the analysis of kulanite. For baricite, however, this method could not be used as the iron present in the mineral oxidizes rapidly during and after grinding. Consequently, although two TGA runs were made, it was found that practically all the iron was in the ferric state. A fresh uncrushed sample analyzed by Dr. E. J. Brooker of X-ray Assay Laboratories gave predominantly ferrous iron. In addition to the two thermogravimetric analyses, an XRF analysis was carried out to determine the amounts of Mg, Fe, and P. Analytical data are summarized in Table 4. These data were treated as follows: (1) because the MgO, Fe₂O₃, and

TABLE 4. CHEMICAL AND THERMOGRAVIMETRIC ANALYSES OF BARICITE

	wt. %
TGA (by D.R. McKinnon): wt. loss in N ₂	28.96
" " O ₂	29.23
XRF (fused sample by B.D. Sturman): MgO	21.7
Fe ₂ O ₃	35.9
P ₂ O ₅	44.2
Total	101.8
Chemical (by E.J. Brooker)	
FeO	19.90
Fe ₂ O ₃	2.77

P₂O₅ were determined on a fused (and oxidized) sample, their percentages are too high. They were reduced by multiplying by 0.7077. This factor is equal to (100 - 29.23)/100, where 29.23 is the weight loss of the mineral in oxygen; (2) the percentage weight loss in nitrogen was taken as the weight percentage of H₂O.

The figures resulting from 1 and 2 above are shown in Table 5 where they are treated as the analysis of oxidized baricite. The amounts of FeO and Fe₂O₃ determined by Dr. E. J. Brooker make it possible to determine the chemical formula of baricite prior to oxidation. His

TABLE 5. ANALYSIS OF OXIDIZED BARICITE.

A	B	C	D	E	F
MgO	15.36	0.3811	Mg 0.3811	1.71 { 3.14 } 1.63 { 3.00 }	MgO 14.64
Fe ₂ O ₃	25.41	0.1591	Fe ³⁺ 0.3182	1.43 { 1.37 } 1.37	Fe ₂ O ₃ 24.37
P ₂ O ₅	31.28	0.2204	P 0.4408	1.98	P ₂ O ₅ 31.62
H ₂ O	28.96	1.6071	H 3.2142	14.42 14.63	H ₂ O 29.37
			O 3.5675	16.00 16.00	
Total	101.01				Total 100.00

A. Corrected weight percentages of constituents. See text for details.

B. Molecular proportions. C. Atomic proportions. D. Number of atoms based on 16 oxygen atoms. E. Idealized number of atoms.

F. Theoretical composition of (Mg_{1.63}Fe_{1.37})₂(PO₄)₂(OH)_{0.15}•6.63H₂O

values of 19.90% FeO and 2.77% Fe₂O₃ are equivalent to 24.88% Fe₂O₃ which is close to the value of 25.41% Fe₂O₃ shown in Table 5. The atomic ratio of Fe²⁺ : Fe³⁺ is 7.98:1. From this ratio and the fact that Mg:(Fe²⁺ + Fe³⁺) = 1.20:1, it follows that Mg:Fe²⁺:Fe³⁺ is 10.78:7.98:1 or, 1.64:1.21:0.15. The general formula for the vivianite group is (R³⁺_{3-x}F³⁺_x)(PO₄)₂(OH)_x•(8-x)H₂O. Expressing the ideal chemical formula of baricite in this form gives:



The theoretical composition of a mineral with this chemical formula is: MgO 14.70, FeO 19.33, Fe₂O₃ 2.66, P₂O₅ 31.56, H₂O 31.75, total 100.00 wt %. The density calculated from the unit-cell parameters and this composition is 2.448g/cm³ which is in good agreement with the measured value of 2.42g/cm³. The specific refractive energy of baricite calculated from the measured refractive indices and density is 0.236. Using the calculated density, it is 0.233. The value calculated from the chemical composition using the constants given by Mandarino (1976) is 0.238.

NOMENCLATURE

Baricite includes all members of the vivianite group in which Mg is greater than any other cation. Type baricite, as described here, is a ferroan baricite. Type material is preserved in the Royal Ontario Museum, Toronto, and in the Mineralosko-Petrografske Muzej in Zagreb, Yugoslavia. The name is pronounced BAR-ICHAIT and is in honor of Prof. Dr. Ljudevit Baric, former Director of the Mineralogical Museum in Zagreb and Professor of Mineralogy at the University of Zagreb.

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