THE CHEMICAL NATURE OF JOAQUINITE

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SUMMARY

Composition $NaBa(Ti,Fe)_3Si_4O_{15}$.

Crystallography: orthorhombic; forms: *c*(001), *p*(111), *m*(110). $a:b:c=0.919:1:2.14$. $a=9.61\text{Å}$, $b=10.45\text{Å}$, $c=22.4\text{Å}$.

Physical Properties: $\alpha=1.748$, $\beta=1.767$, $\gamma=1.823$. Bx (+). $2V=50°\pm$. $\rho<v$. $X=a$, $Y=b$, absorption $Z>Y>X$. G.=3.89. $H=5\frac{1}{2}\pm$. Color, honey yellow to brown.

The mineral joaquinite was first recorded by Louderback* in 1909. It occurs in minute amounts associated with benitoite and neptunite in the unique deposit of these unusual titanosilicates in San Benito County, California. Scarcity of material made it impossible for Louderback to make any but microchemical tests on the tiny crystals and he supposed joaquinite to be a titanosilicate of calcium, possibly a dimorphic form of titanite. It was correctly designated as orthorhombic in crystallization but nothing has since been added to the original incomplete description.

Sufficient material for a fuller investigation was finally secured by working over large amounts of material from this locality. The veins containing the associated minerals are filled in large part by massive natrolite. Several hundred pounds of the vein material was secured and subjected to the action of hydrochloric or sulphuric acid to dissolve the natrolite. This laborious process yielded specimens with variable amounts of neptunite and benitoite and about 10 per cent of them showed more or less joaquinite. By scraping off every visible crystal and by collecting and washing the gelatinous sediment in the acid jars, something less than a gram of pure material was finally obtained. It may be said in passing that the thousands of crystals of benitoite and neptunite revealed on these specimens added no new facts regarding their crystallography to those already described.

The joaquinite crystals are always small, the largest seen measuring not more than 2 mm. in maximum diameter. They are generally attached to the wall of the vein, like the majority of neptunite and benitoite crystals; but a few were completely enclosed in the natrolite and in one or two cases were implanted on or surrounded by benitoite. The three titanium minerals then show no

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* Louderback, G. D., Benitoite: *Bull. Univ. of Calif., Dept. of Geology*, **5**, 1909, 376.

marked sequence in time of deposition. Isolated crystals are the rule; the specimen shown in the photograph, fig. 2, was the only one of several hundred obtained which showed more than an occasional crystal.

Joaquinite is orthorhombic, showing only the forms *c*(100), *p*(111), and rarely *m*(110). The habit varies from pyramidal with a tiny facet of the base, to flat tabular parallel to the base as shown in the two figures.

The crystals are always striated and are often in subparallel aggregates; so that although hundreds of crystals were examined none was found which gave satisfactory signals on the goniometer, images being multiple or confused. By selecting the brightest image of the chain of signals which often extended over several degrees of ρ angle the following fairly consistent readings were obtained on three crystals:

Table I

Angles of Joaquinite

Crystal 1.	ϕ	ρ	Crystal 3.	ϕ	ρ
	47° 24′	73° 31′		47° 17′	73° 20′
	26	33		19	24
	14	39		13	19
	46 57	40		11	55
			Average	47 17	73 27
Crystal 2.	47 16	73 12			
	20	21			
	15	16			
	13	29			

Taking this form as (111) the coordinate angles yield the elements

$$p_0=2.47 \qquad q_0=2.28$$
$$a:b:c=0.923:1:2.28$$

Another axial ratio was obtained by the measurement of unit cell dimensions from *x*-ray photographs which were obtained by the rotation of crystals about each of the three crystallographic axes. The range of values obtained is shown in Table II.

Table II.

For the *a*-axis rotation		For the *b*-axis rotation	
Layer line	Axis length (Å)	Layer line	Axis length (Å)
1	9.72	2	10.6
2	9.86	3	10.6
3	9.58	4	10.4
4	9.58	5	10.4
5	9.47	6	10.3
6	9.58	7	10.3

For the c-axis rotation

Layer line	Axis length (Å)
1	22.9
2	22.9
3	22.9
4	22.2
5	22.2
6	22.2
7	22.2
8	23.7
9	22.2
11	22.9

The weighted average values thus derived are:
axis $a=9.61$ Å; axis $b=10.45$ Å; axis $c=22.4$ Å from which are calculated

$$p_0=2.33 \qquad q_0=2.14$$
$$a:b:c=0.919:1:2.14$$

Calculating coordinate angles for (111) from these axes we obtain

$$\phi=47^\circ\ 25' \qquad \rho=72^\circ\ 29'$$

By measurement

$$\phi=47^\circ\ 17' \qquad \rho=73^\circ\ 27'$$

The agreement is good for ϕ but very poor for ρ. Since the x-ray values are based on a larger number of measurements which are in this case at least as accurate as those obtained by goniometric methods, the latter values are adopted.

Physical Properties

The indices of refraction and other optical properties were measured by the immersion method with the following results:

$\alpha=1.748$ (+) $2V=50^\circ$
$\beta=1.767$ $\rho<v$ perceptible
$\gamma=1.823$

The orientation is as given by Louderback

$$X=a,\ Y=b,\ Z=c$$

Absorption in yellow slight with $Z>Y>X$.
Color, honey yellow to brown.

The density as measured by floating in Clerici solution is 3.89.

Applying the formula $\frac{n-1}{d}=K$ to joaquinite there is apparently a large discrepancy between the K value as determined from

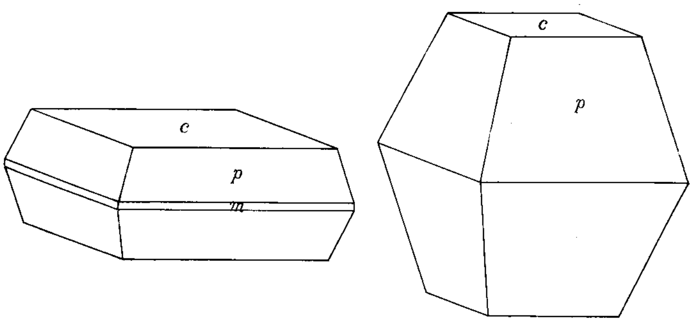

FIG. 1. Crystals of Joaquinite, San Benito Co., Calif.

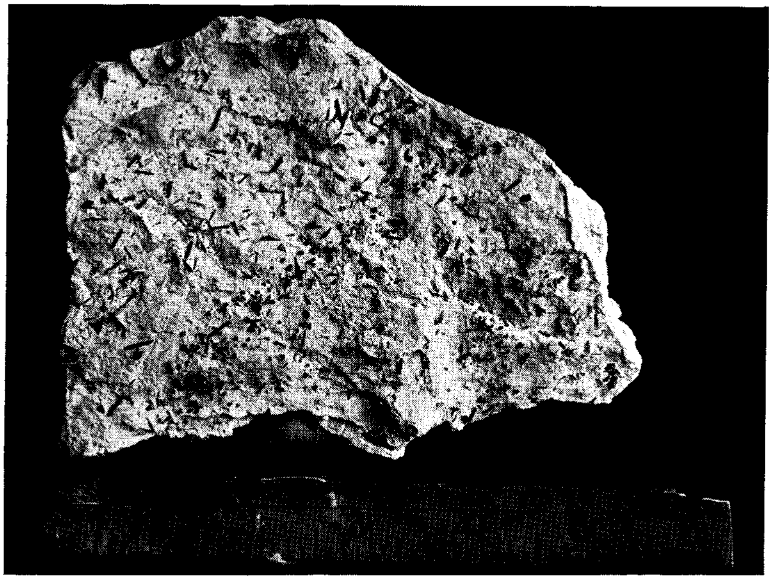

FIG. 2. Photograph of a specimen of joaquinite. The black dots are joaquinite crystals, the needles neptunite, the triangular crystals, benitoite. San Benito Co., Calif.

the physical constants, and the value as determined from the composition.

$$\text{For}\ \frac{n-1}{d}=K=\frac{.775}{3.89}=.199$$

whereas K from the composition is .244. This large discrepancy can not be ascribed to error in determination of either n, the mean index of refraction, or d, the density, since these two values are determinable well within the limit of error indicated. It seems improbable that the refractive energy constants (K) used in this computation are much in error since an application of this law to benitoite, which contains essentially the same oxides, yields a satisfactory agreement. There are left then the possibilities that the titanium oxide, as given in the analysis, is really in another state of oxidation and consequently has a different K value, or that some rare element with a fairly low K value (0.265) is present in joaquinite, and has been determined as TiO_2, due to the very small sample available for analysis.

Composition of Joaquinite
Analyses by W. F. Foshag

	I	II	III	IV	V
SiO_2	37.37	35.27		36.4	36.3
TiO_2	32.03	29.53		30.5	32.0
FeO	3.17	3.41		3.5	3.8
BaO	23.13	23.91		24.7	23.2
CaO	0.29	0.27			
MgO	0.39	0.07		.3	
Ign.	0.91	0.47			
Na_2O			4.47	4.6	4.7
				100.0	100.0

I. Preliminary qualitative-quantitative analysis, 0.2071 grams.
II. Analysis on 0.1500 grams, FeO on 0.1012 grams.
III. Average of 2 samples, 0.1016 grams and 0.1698 grams.
IV. Average composition computed from II and III reduced to 100 per cent.
V. Calculated from formula Na Ba (Ti, Fe)$_3$ Si$_4$O$_{15}$.

The Number of Molecules in the Unit Cell

From the axial lengths determined by rotation x-ray photographs, the volume in the unit cell is found to be $(9.61\times10^{-8})\times(10.45\times10^{-8})\times(22.4\times10^{-8})=2250\times10^{-24}$.

Substituting this in the relation

$$mM=dV$$

where m = number of molecules in unit cell

M = molecular weight $\times(1.65\times10^{-24})$

d = density, 3.89

V = volume of unit cell $=2250\times10^{-24}$

for $M=1324\times(1.65\times10^{-24})$ in the formula Na Ba (Ti, Fe)$_3$Si$_4$O$_{15}$ the value for $m=4$. There are, therefore, 4 molecules of composition Na Ba (Ti, Fe)$_3$Si$_4$O$_{15}$ in the unit cell of joaquinite.

The somewhat unsatisfactory results of this investigation of joaquinite, due at least in part to the small amount of material secured, seem disproportionate to the large amount of work involved. The senior author feels it his duty to give credit to hi co-s workers whose efforts made the study possible. The first lot of material worked was secured by Mr. Wilke of Palo Alto who made the long trip to the mine to collect it. The seventy-five pounds of vein specimens he shipped to us in 1927 was worked up by Lyman W. Lewis who spent several weeks treating it with acid, repeatedly washing away the gelatinous silica set free from the natrolite by the acid and then collecting and purifying the few crystals obtained. The fruit of his labor was 0.7 grams of nearly pure material and the analysis of this first sample was not satisfactory. The writer visited the locality in 1929 and shipped back another lot of about 200 pounds of specimens. These in turn were treated by Mr. Berman with a like expenditure of weeks of labor and a product of 0.3 grams of pure material. He also made the x-ray study of the crystals and did part of the crystal measurement.