American Mineralogist
Vol. 57, pp. 85–102 (1972)

CHEMICAL COMPOSITION AND PHYSICAL, OPTICAL, AND STRUCTURAL PROPERTIES OF BENITOITE, NEPTUNITE, AND JOAQUINITE[1]

JO LAIRD AND ARDEN L. ALBEE, *Division of Geological and Planetary Sciences, California Institute of Technology*
Pasadena, California 91109

ABSTRACT

The chemical composition, density, optical properties, and cell parameters of benitoite, neptunite, and joaquinite from San Benito County, California, are reported. Electron microprobe analyses show that benitoite is homogeneous, stoichiometric $BaTiSi_3O_9$. Electron microprobe and emission spectrographic data indicate that neptunite is fairly homogeneous and that its formula is $Li_{0.6}Na_{2.1}K_{0.9}(Fe,Mg,Mn)_{2.0}Ti_{2.0}Si_{8.0}O_{24}$. Joaquinite is quite complicated chemically, containing hydroxyl and 15–20 weight percent rare earth oxides. The density and optical properties for each mineral and cell parameters for benitoite and neptunite are similar to those given in the literature. Weissenberg and precession X-ray diffraction data indicate that single crystals of joaquinite have varying proportions of a monoclinic and an orthorhombic component. The orthorhombic unit cell has parameters $a = 10.48$ (2) Å, $b = 9.66$ (2) Å, and $c = 22.26$ (2) Å; the monoclinic unit cell has parameters $a = 10.51$ (2) Å, $b = 9.66$ (2) Å, $c = 11.82$ (2) Å, and $\beta = 109.5$ (2)°. Structural, chemical, and infrared data suggest the following formula for joaquinite:

$$Ba_{8.1}(Sr_{1.7}RE_{6.5}Th_{0.1})\ (Ca_{0.2}Na_{3.3}Fe_{3.1}Li_{0.8}Mg_{0.1})\ Ti_{8.1}Si_{32.0}O_{98.7}(OH)_{13.3}.$$

INTRODUCTION

The three rare minerals benitoite, neptunite, and joaquinite occur in natrolite veins which cut a glaucophane schist inclusion in a serpentinite body near New Idria, San Benito County, California. Louderback and Blasdale (1909) described this occurrence in detail; they gave wet chemical analyses for benitoite and neptunite and physical and optical properties for all three minerals. No further chemical data for benitoite have been reported. Benitoite is of crystallographic interest because it is the only known member of the ditrigonal-dipyramidal symmetry class; its structure was determined by Zachariasen (1930). Recently, Fischer (1969) refined the crystal structure of benitoite and confirmed Zachariasen's (1930) results.

Wet chemical analyses of neptunite from this locality were given by Bradley (1909) and more recently by Cannillo, Mazzi, and Rossi

---

[1] Contribution number 1979.

(1966). A summary of the optical properties and geologic occurrences of neptunite was given by Heinrich and Quon (1963). Berry (1963) and Cannillo *et al.* (1966) reported crystal structure data for San Benito neptunite.

Palache and Foshag (1932) determined the physical and crystallographic properties and chemical composition of California joaquinite. Other occurrences of joaquinite have been discussed by Bell (1963) and Semenov, Bukin, Balashov, and Sørensen (1967). Semenov *et al.* (1967) found 22.59 weight percent $(RE)_2O_3$ (rare earth oxides) in joaquinite from southern Greenland and suggested that there were different minerals of the joaquinite group; they also reported 11.5 and 15.0 percent $(RE)_2O_3$ in two samples of joaquinite from California but did not give complete chemical analyses. All the published work on joaquinite has reported it as orthorhombic. However, J. E. Rowland (written communication from E. H. Nickel, 1970) has found joaquinite from San Benito County with a monoclinic unit cell.

The purpose of this work was to determine the complete chemical composition and other properties of benitoite, neptunite, and joaquinite from San Benito County, California. A secondary objective was to determine whether the electron microprobe techniques used in this laboratory could be employed successfully to analyze such a complex mineral as joaquinite.

ANALYTICAL TECHNIQUES

Electron microprobe analyses were made with a three-channel Applied Research Laboratory model EMX microprobe using the techniques of Bence and Albee (1968) and Albee and Ray (1970). The accelerating voltage was 15 kv at all times; and the beam current, pulse height selection, spot size, and counting time were constant for each element analyzed but adjusted for each element and mineral to obtain maximum counting rates with minimum sample damage and contamination. Simple silicates and oxides were used as standards for the major elements; the rare earth elements of joaquinite were analyzed relative to apatite, thalenite, and monazite. Ba and Ti in benitoite were analyzed relative to Ba-feldspar and synthetic rutile, respectively; whereas, Ba and Ti in neptunite and joaquinite were analyzed relative to benitoite, assuming stoichiometry for the benitoite. Previous studies in this laboratory indicate an accuracy for common elements constituting more than about one weight percent of the sample of about two percent of the amount present. Standards and correction parameters for less common elements are not as good, and their abundance in joaquinite somewhat decreases the accuracy for the common elements.

The emission spectrographic analyses are an average of duplicate burns (except for the joaquinite samples, which were only run once because of the small amount of sample available) on a 3.4 m Wadsworth-mount spectrograph with a 15,000 line per inch diffraction grating. A D.C. arc with a 19 amp short circuit was used. The samples were diluted in the proportions: 1.0 sample, 0.1 Na_2CO_3, 0.5

graphite, and 0.9 quartz. For benitoite and neptunite 25 mg of this mixture were weighed into the electrode and burned to completion; for joaquinite 10 mg were used.

X-ray diffraction powder work was done in a Guinier camera using quartz-monochromatized Cu Kα radiation. Single-crystal work was done in Supper Weissenberg and precession cameras with Fe Kα and Mo Kα radiation, respectively. The unit cell dimensions for benitoite and neptunite were calculated by a least squares technique using previously indexed lines; 44 lines were fitted for benitoite and 34 for neptunite. Indices were calculated for benitoite from the cell parameters of Fischer (1969) and for neptunite from the paramenters of Berry (1963).

The densities were determined on a Roller-Smith Berman balance using toluene. For benitoite and neptunite determinations were made on individual grains, weighing from 4–40 mg, and averaged. Because of the limited amount of material available, the density of joaquinite was determined by weighing 2–4 mg samples composed of several grains three times. Indices of refraction were determined with Na light and index oils calibrated with a Zeiss Abbé refractometer. Those indices which were matches with the oils are cited as accurate to 0.001; indices bracketed by two oils are cited as accurate to 0.002.

The infrared spectrum of joaquinite was measured on a Perkin-Elmer 225 infrared spectrophotometer using a KBr pellet, 1.5 mg sample to 400 mg KBr. The spectrum was normalized to that of a similar 400 mg KBr pellet, prepared simultaneously, in the reference beam.

Benitoite, neptunite, and joaquinite were analyzed from five samples from the California Institute of Technology collection. Benitoite was chipped from sample D4, neptunite from samples D2636 and D6794, and joaquinite from samples D2200, D7574, and D4. Joaquinite was taken from sample D6794 by dissolving the enclosing natrolite in concentrated HCl. In order to obtain chemical data consistent with other properties, densities, optical properties, and cell parameters were determined on grains of the same samples that were used for the chemical analyses.

Results and Discussion

Benitoite

The chemical composition of benitoite is delineated in Table 1. Benitoite may be blue or white to colorless. Both colors occur within single crystals and are separated by distinct contacts. Louderback and Blasdale (1909) suggested a systematic relationship between color change and crystallographic axes, but no systematic and consistent relationship was apparent in the crystals available to us.

The SiO_2, BaO, and TiO_2 contents of blue benitoite (analysis 1) are virtually identical to those of white benitoite (analysis 2) from the same crystal and closely approach the stoichiometric composition of $BaTiSi_3O_9$ (SiO_2, 43.59 percent; TiO_2, 19.32 percent; BaO, 37.09 percent). Our results are similar to the original analyses for blue and white benitoite by Louderback and Blasdale (1909) (Table 1, analyses 3 and 4) but do not support their reported differences in TiO_2 and BaO. Standard deviations for the averages of the individual analyses are less than half a percent, indicating both the blue and the white benitoite are homogeneous (see also Figure 1).

Electron beam scans and analytical profiles across color contacts indicate no detectable variation in compostion for Ba, Ti, and Si. Emission spectrographic analyses were made to see if differences existed below the sensitivity of the electron microprobe (see Table 1). Although they show only small differences in the trace element contents of the blue and white benitoite, the difference in iron content may be significant.

Table 1. Chemical Analyses of Benitoite, San Benito County, California

	1			2			3	4
	Microprobe		E.S.[a]	Microprobe		E.S.[a]		
	Wt. %	Formula[b]	Wt. %	Wt. %	Formula[b]	Wt. %	Wt. %	Wt. %
SiO_2	43.10	2.98	----	42.62	2.97	----	43.68	43.61
Al_2O_3	d		0.2	d		0.04	----	----
TiO_2	19.51	1.01	----	19.44	1.02	----	20.09	19.50
FeO[c]	d		0.05	d		0.01	----	----
MgO	d		Trace	d		Trace	----	----
CaO	d		0.1	d		0.006	----	----
BaO	37.23	1.01	Major	37.27	1.02	Major	36.33	37.01
Na_2O	0.13	0.02	----	0.14	0.02	----	----	----
Nb	d		----	d		0.14	----	----
Sr	d		0.0035	d		0.0025	----	----
V	d		0.0015	d		0.001	----	----
Zr	d		0.012	d		0.08	----	----
Total	99.97			99.47			100.10	100.12

[a] Emission spectroscopy analysis by E. Bingham. Looked for but not found: Ag, As, Au, B, Be, Bi, Cd, Ce, Co, Cr, Cu, Ga, Gd, La, Mo, Mn, Nd, Ni, Pb, Pt, Sb, Sc, Sn, Ta, Th, Tl, W, Y, Yb, and Zn.

[b] Cation formula proportion determined by normalizing anhydrous oxygen to 9.

[c] Total Fe as FeO.

[d] Less than the sensitivity of a wavelength scan (~ 0.10 wt. percent).

1. D4, blue color. Microprobe analysis is the average of 6 points.
2. D4, white color. From the same crystal as (1). Microprobe analysis is the average of 6 points.
3. Blue color. Louderback and Blasdale (1909).
4. White color. Louderback and Blasdale (1909).

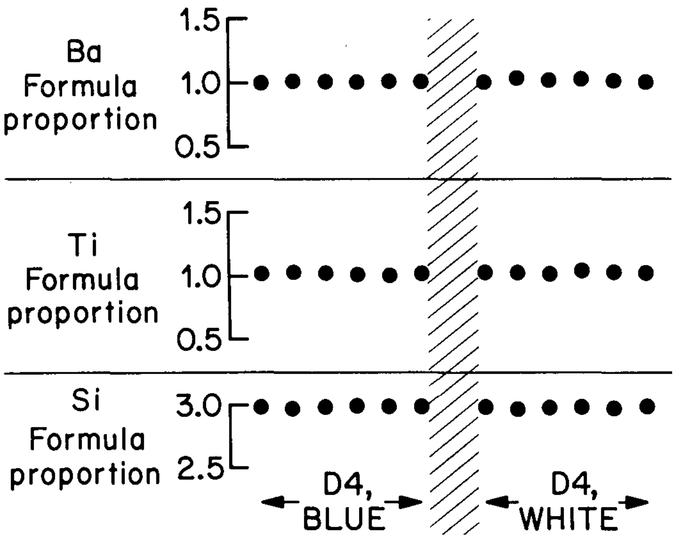

FIG. 1. Scatter diagram for the cation formula proportions of benitoite samples from San Benito County, California. Each point represents a complete microprobe analysis. Formula proportions are determined by normalizing the analyses to anhydrous oxygen = 9.

Benitoite has very intense cathodoluminescence under the electron beam and is commonly used by microprobe operators to check beam size and shape. Many of these operators have found that benitoite contains no detectable elements other than Ba, Ti, Si, and O and have used it is a microprobe standard assuming stoichiometry.

The density of benitoite is 3.64(2) gm/cc; it is uniaxial positive with $\omega = 1.756(1)$ and colorless and $\epsilon = 1.800(1)$ and blue. Louderback and Blasdale (1909) reported $\rho = 3.64\text{–}3.67$ gm/cc, $\omega = 1.757$, and $\epsilon = 1.804$.

From single-crystal work on benitoite from San Benito County, Fischer (1969) reported that benitoite is hexagonal with the space group $P\bar{6}c2$; $a = 6.6410$ (7) Å and $c = 9.7597$ (10) Å. A Guinier X-ray powder pattern gives $a = 6.63$ (1) Å and $c = 9.73$ (1) Å. The *d*-spacings are in good agreement with the ASTM index.

Neptunite

Chemical data for neptunite are summarized in Table 2. The microprobe analyses are similar to those reported in the literature except that Cannillo *et al.* (1966) reported 1.63 percent Li_2O. It is impossible to analyze for lithium with the microprobe because of its low atomic number; however, our analytical totals are one percent low, and qualitative emission spectroscopic data indicate 1–2 percent Li_2O. The formula $LiNa_2K(Fe,Mg,Mn)_2\,(TiO)_2\,(Si_8O_{22})$ was suggested for neptunite by Cannillo *et al.* (1966). In the absence of Al, the formula proportions can be calculated from the analyses by normalizing Si to 8. Our analyses normalized in this manner give $Li_{0.6}Na_{2.1}K_{0.9}\,(Fe,Mg,Mn)_{2.0}\,Ti_{2.0}Si_8O_{24}$. This formula is also obtained from the analyses by normalizing total cation charges (exclusive of Li) to 47 or total cations (exclusive of Li) to 15. The formula proportion of Li

Table 2. Chemical Analyses of Neptunite, San Benito County, California

	1			2			3	4	5
	Microprobe		E.S.[a]	Microprobe		E.S.[a]			
	Wt. %	Formula[b]	Wt. %	Wt. %	Formula[b]	Wt. %	Wt. %	Wt. %	Wt. %
SiO_2	53.96	8.00	----	54.09	8.00	----	53.44	52.87	52.29
Al_2O_3	d		0.04	d		0.1	----	----	----
TiO_2	17.74	1.98	----	17.99	2.00	----	17.18	17.83	17.35
FeO	11.71[c]	1.45	8[c]	10.75[c]	1.33	10[c]	11.23	11.69	11.92
MnO	1.40	0.18	1.5	1.65	0.21	1.3	1.78	0.85	2.27
MgO	1.73	0.38	1.2	2.16	0.48	1.2	1.82	1.44	1.55
CaO	d		0.02	d		0.04	0.25	1.56	0.62
BaO	0.25	0.01	0,06	0.18	0.01	0.06	----	----	----
Na_2O	7.38	2.12	----	7.51	2.15	----	9.14	9.56	6.81
K_2O	4.84	0.92	----	4.76	0.90	----	5.39	5.08	5.58
Li_2O	e	0.59[f]	1-2	e	0.54[f]	1-2	----	----	1.63
Ag	d		0.0003	d		0.0002	----	----	----
Cr	d		0.0023	d		0.0048	----	----	----
Co	d		0.01[g]	d		0.014[g]	----	----	----
Nb	d		< 0.01	d		< 0.01	----	----	----
Ni	d		0.0028	d		0.0038	----	----	----
V	d		0.005	d		0.006	----	----	----
Zr	d		0.0065	d		0.0054	----	----	----
Total	99.01			99.09			100.23	100.88	100.02

[a] Emission spectroscopy analysis by E. Bingham. Looked for but not found: As, Au, B, Be, Bi, Cd, Cu, Ga, La, Mo, Pb, Pt, Sb, Sc, Sn, Sr, Ta, Th, Tl, W, Y, Yb, and Zn.

[b] Cation formula proportion determined by normalizing Si to 8.

[c] Total Fe as FeO.

[d] Less than the sensitivity of a wavelength scan (~ 0.10 wt. percent).

[e] Cannot determine with the microprobe.

[f] Calculated by assigning the deficiency in the analytical total from 1.00 to Li_2O.

[g] Possible interference.

1. D2636. Microprobe analysis is the average of 12 points on 7 grains.
2. D6794. Microprobe analysis is the average of 7 points on 4 grains.
3. Louderback and Blasdale (1909).
4. Bradley (1909).
5. Cannillo, et al. (1966).

in the analyses is calculated by assigning the deficiency of the analytical total from 100 percent to Li_2O; if the totals are about half a percent high, the formula proportion of Li would be 1.

In the reported analyses (Table 2), iron is given as FeO. Bancroft, Burns, and Maddock (1967) have determined from Mössbauer spectroscopy on neptunite from California that at least 95 percent of the iron is present as Fe^{2+}, corroborating the formula given above.

Figure 2 is a scatter diagram of the cation formula proportions of neptunite for each point analyzed with the microprobe. Although there is a scatter in the Fe, Mg, and Mn contents of single points, the total Fe+Mg+Mn proportion is constant. Electron beam scan photographs also show that neptunite is quite homogeneous.

The density and optical properties of neptunite agree well with those reported in the literature for this and other occurrences. The density is 3.20 (2) gm/cc compared with the values 3.19–3.23 gm/cc listed in Murdoch and Webb (1948). Optical properties of neptunite determined on sample D6794 are as follows: $2V$ (+) ~40°; optic plane $\parallel$ (010); $y = b$; $Z \wedge c = 17°$; $\alpha = 1.692(1)$, pale yellow; $\beta = 1.702$ (1), yellow orange; and $\gamma = 1.734(2)$, red orange to red brown.

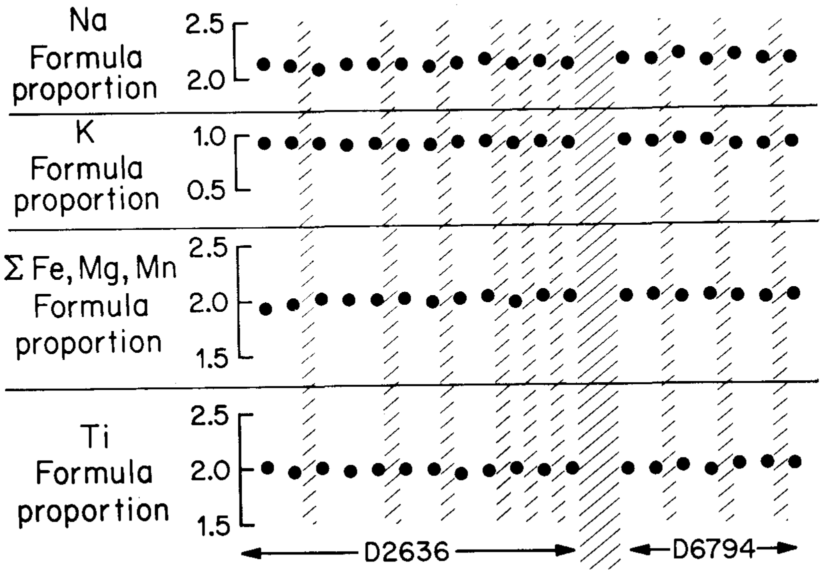

FIG. 2. Scatter diagram for the cation formula proportions of neptunite samples from San Benito County, California. Each point represents a complete microprobe analysis, and analyses for each grain are grouped on the figure. Formula proportions are determined by normalizing the analyses to Si = 8.

Those reported by Larsen and Berman (1934) on California (?) neptunite are: 2V = 49°, Z ∧ c = 16°, $\alpha = 1.690$, $\beta = 1.699$, and $\gamma = 1.736$.

Cannillo *et al.* (1966) proposed that neptunite is monoclinic, space group *Cc*, but reported no new cell parameters. Guinier powder data on neptunite from sample D6794 give cell dimensions and *d*-spacings similar to those reported by Berry (1963). Our parameters are $a = 16.48(3)$ Å, $b = 12.49(2)$ Å, $c = 10.00(2)$ Å, and $\beta = 115.4(1)°$; Berry (1963) reported $a = 16.7$ Å, $b = 12.4$ Å, $c = 10.0$ Å, and $\beta = 115°44'$ from single-crystal precession photographs.

Joaquinite

The density of the joaquinite from sample D6794 is 3.98(5) gm/cc, compared with 3.89 gm/cc given by Palache and Foshag (1932). Our data indicate that joaquinite is biaxial positive with a range in 2V from ~30–55°. The indices are: $\alpha = 1.753(1)$, $\beta = 1.767$ (1), and $\gamma = 1.822(2)$; α and β are colorless and γ is pale yellow. Palache and Foshag (1932) reported $2V = 50°$, $\alpha = 1.748$, $\beta = 1.767$, and $\gamma = 1.823$.

The chemical composition of joaquinite is complex; electron microprobe and emission spectroscopy data are presented in Table 3 with other chemical data on joaquinite taken from the literature. Thirty-eight points on 15 grains of 4 samples were analyzed with the microprobe. Many grains are inhomogeneous, but joaquinite from sample D6794 is quite homogeneous; all of our data on the density and optical and structural properties of joaquinite were determined on grains of this sample.

The infrared spectrum of joaquinite is presented in Figure 3. The sharp bands at ~3500 and 3560 cm^{-1} indicate that the joaquinite structure includes significant quantities of crystallographically-ordered hydroxyl groups. The band at ~1610 cm^{-1} (corresponding to an HOH bending motion) and the broad absorption feature centered at ~3400 cm^{-1} (the OH stretch) are probably due to water adsorbed during sample handling procedures. The C-H bands around 2900 cm^{-1} are due to organic impurities introduced during sample handling. In this spectrum the lower energy region is dominated by the strong Si-O absorption near 1000 cm^{-1}. However, infrared spectroscopic data on silicate minerals is insufficient to assign this Si-O absorption pattern to a particular type of silicate.

We are unable to determine directly the amount of H_2O that is present in joaquinite because of the small amount of material available and the small size of the crystals. The reported H_2O content is based on the difference between the analyzed oxide total and 100 percent and may not be very accurate. Qualitative emission spectrographic analyses indicate that Li is present but in an amount less than 1 percent Li_2O. There may be some Fe_2O_3, although Semenov *et al.* (1967) reported only 0.39 percent Fe_2O_3 in joaquinite from southern Greenland. The presence of these components will affect the value reported as H_2O.

The number of rare earth elements present in joaquinite makes it difficult to do accurate microprobe analyses because their peaks are close together. However, total rare earth oxide concentration determined by electron microprobe and by emission spectroscopic analyses differs by only 0.5 weight percent for sample D6794 and by 2 weight percent for sample D2200. Total rare earth oxide concentration in the 38 microprobe analyses of joaquinite ranges from 15–20 weight percent; this is zero to 8.5 weight percent higher than that reported by Semenov *et al.* (1967) for two samples of joaquinite from California (see Table 3).

Joaquinite is listed in the literature as orthorhombic. However, J. F. Rowland has found a monoclinic crystal from the California locality (E. H. Nickel, written communication, 1970). Single-crystal

Table 3. Chemical Analyses of Joaquinite

	1			2			3		4		5	6	7	8
	Microprobe		E.S.[a]	Microprobe		E.S.[a]	Microprobe		Microprobe					
	Wt. %	Formula[b]	Wt. %	Wt. %	Formula[b]	Wt. %	Wt. %	Formula[b]	Wt. %	Formula[b]	Wt. %	Wt. %	Wt. %	Wt. %
SiO_2	34.97	32.00	----	35.17	32.00	----	35.17	32.00	34.93	32.00	36.4	----	----	33.82
TiO_2	11.83	8.14	----	12.24	8.37	----	11.41	7.81	11.90	8.21	30.5	----	----	9.20
Fe_2O_3											----	----	----	0.39
FeO	4.09[c]	3.13	----	3.76[c]	2.86	----	4.55[c]	3.46	4.35[c]	3.33	3.5	----	----	4.78
MnO	0.00		----	0.08	0.06	----	0.06	0.05	0.00		----	----	----	0.70
MgO	0.05	0.07	----	0.09	0.12	----	0.32	0.43	0.16	0.21	0.3	----	----	----
BaO	22.44	8.05	----	22.36	7.97	----	21.99	7.84	22.50	8.08	24.7	18.0	18.1	21.46
CaO	0.21	0.20	----	0.32	0.31	----	0.45	0.44	0.38	0.37	----	----	{ 8.1	{ 0.03
SrO	3.20	1.70	----	3.84	2.03	----	3.36	1.77	3.54	1.88	----	----		
Na_2O	1.87	3.32	----	1.75	3.09	----	1.81	3.19	1.82	3.24	4.6	----	----	2.41
K_2O	0.03	0.04	----	0.04	0.05	----	0.04	0.05	0.03	0.03	----	----	----	0.22
Li_2O	e		< 1	e		< 1	e		e		----	----	----	----
ThO_2	0.27	0.06	----	0.84	0.17	----	0.63	0.13	0.76	0.16	----	----	----	0.38
Nb_2O_5	d		----	d		----	d		d		----	----	----	2.31
Ce_2O_3	10.69	3.58	8.2	9.91	3.30	8.2	11.32	3.77	11.51	3.86	----	6.8	5.6	9.40
Dy_2O_3	0.21	0.06	0.2	0.21	0.06	< 0.2	0.19	0.06	0.05	0.02	----	----	0.1	----
Er_2O_3	0.00		0.1	0.06	0.02	< 0.1	0.03	0.01	0.02	0.01	----	----	0.1	----
Gd_2O_3	0.26	0.08	1	0.14	0.04	0.8	0.05	0.02	0.00		----	----	0.3	----
La_2O_3	2.14	0.72	3.0	2.52	0.85	2.9	2.82	0.95	2.99	1.01	----	3.6	2.3	10.05
Nd_2O_3	3.21	1.05	3.5	2.82	0.92	2.7	2.37	0.77	1.87	0.61	----	3.2	2.1	2.15
Pr_2O_3	1.25	0.42	1.5	1.17	0.39	0.4	1.13	0.37	1.06	0.35	----	1.0	0.6	0.99
Sm_2O_3	0.70	0.22	0.7	0.58	0.18	0.4	0.36	0.11	0.17	0.05	----	0.1	0.4	----
Tm_2O_3	d		< 0.02	d		< 0.04	d		d		----	----	----	----
Y_2O_3	0.70	0.34	0.5	0.33	0.16	0.1	0.26	0.13	0.06	0.03	----	0.3	----	----
ΣRE_2O_3	19.16	6.47	18.7	17.74	5.92	15.8	18.53	6.19	17.73	5.94		15.0	11.5	22.59
H_2O	e	11.49[f]		e	10.75[f]		e	10.21[f]	e	11.62[f]	----	----	----	1.50
F	d			d			d		d		----	----	----	0.38
$-O=F_2$														0.16
Total	98.12			98.23			98.32		98.10		100.0			100.01

a Emission spectroscopy analysis by E. Bingham. b Cation formula proportion determined by normalizing Si to 32. c Total Fe as FeO.
d Less than the sensitivity of a wavelength scan (~ 0.10 wt. percent). e Cannot determine with the microprobe.
f Calculated by assigning the deficiency in the analytical total from 1.00 to H_2O.
1. D6794, San Benito County, California. Microprobe analysis is the average of 6 points on 5 grains.
2. D2200, San Benito County, California. Microprobe analysis is the average of 21 points on 7 grains.
3. D7574, San Benito County, California. Average of 6 points on 2 grains.
4. D4, San Benito County, California. Average of 5 points on 1 grain.
5. San Benito County, California. Palache and Foshag (1932). Analysis reduced to 100 percent.
6. San Benito County, California. Semenov, et al. (1967).
7. San Benito County, California. Semenov, et al. (1967).
8. S. Greenland. Semenov, et al. (1967).

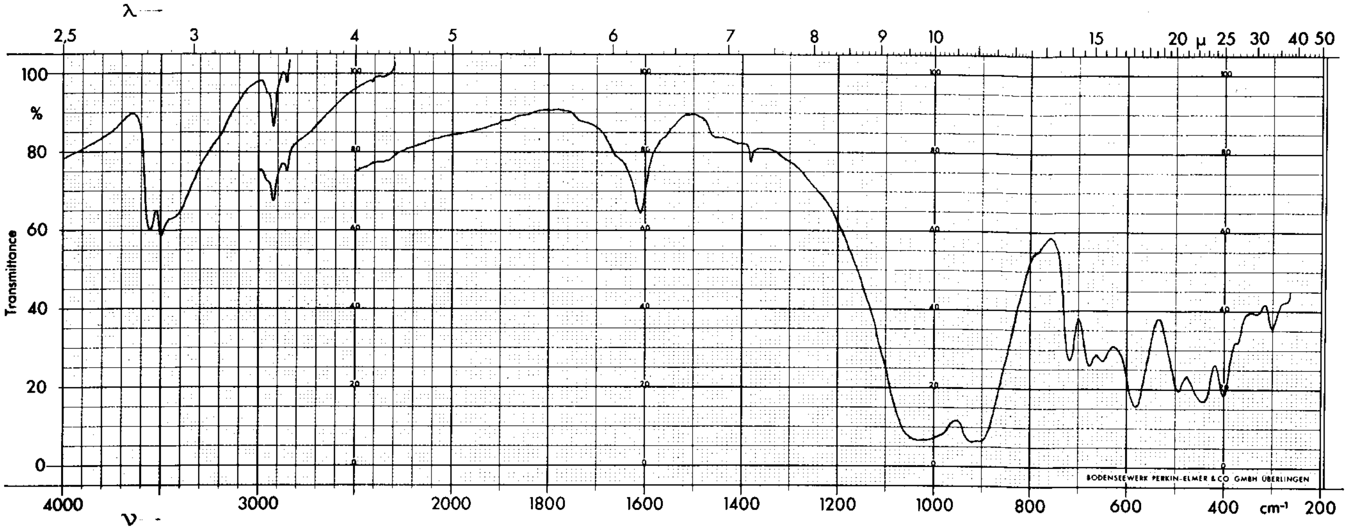

FIG. 3. Infrared spectrum of joaquinite from sample D6794 from San Benito County, California.

X-ray diffraction work was undertaken in order to resolve this problem; the results of this study and the structural data in the literature for joaquinite are delineated in Table 4.

Precession and Weissenberg photographs on a crystal of joaquinite from sample D6794 show it to be monoclinic with cell dimensions $a_m = 10.51(2)$ Å, $b_m = 9.66(2)$ Å, $c_m = 11.82(2)$ Å, and $\beta = 109.5(2)°$. Another crystal of joaquinite from sample D6794 gives an apparently orthorhombic diffraction pattern corresponding to cell dimensions $a_o = 10.48(2)$ Å, $b_o = 9.66(2)$ Å, and $c_o = 22.26(2)$ Å. Because the *a* and *b* axes are closely similar for the monoclinic and orthorhombic cells and because $c_o = 2c_m \sin \beta$ to a close approximation, the possibility must be considered that the apparently orthorhombic diffraction pattern is the result of twinning of monoclinic individuals. As shown in Figure 4, the monoclinic reciprocal lattice points $4n, k, l$ correspond very closely (if not exactly) with points of the orthorhombic reciprocal lattice; in fact, all of the $4n, k, l$ reflections observed in the orthorhombic pattern can be explained by twinning of the monoclinic lattice on (001). However, reflections with $h \neq 4n$ do not coincide in the two reciprocal lattices; hence, the complete orthorhombic pattern cannot be explained by twinning of the known monoclinic cell. We conclude that joaquinite occurs in two crystalline modifications that are very closely related but are quite distinct.

As shown in Figure 4, the monoclinic cell is related to the orthorhombic one by the conditions $a_o \approx a_m$, $b_o \approx b_m$, and $c_m^* \approx 2\,c_o^* \approx 8/3\,a_o^* \cot \beta^*$. The last condition follows from the interesting coincidence of the $80\bar{3}$ reflection in the monoclinic reciprocal lattice and the 800 reflection in the orthorhombic reciprocal lattice. The value of β calculated from the last condition and the measured axial lengths is 109.4°, as compared with the directly measured $\beta = 109.5°$.

The orthorhombic cell found here agrees with the parameters reported by Palache and Foshag (1932), Bell (1963), and Semenov *et al.* (1967). Because of its close relation with the monoclinic cell, we have chosen the orthorhombic axes to correspond with those of the monoclinic cell. Therefore, in Table 4 the *a* axis of earlier workers is redefined as b_o and the *b* axis as a_o.

Systematic extinctions for the monoclinic crystal indicate possible space groups *C2*, *Cm*, or *C2/m*; the orthorhombic crystal may belong to space group *Cc2m*, *Ccm2*, or *Ccmm*.

Diffraction patterns from the monoclinic crystal show additional weak, somewhat diffuse reflections in positions corresponding to reflections from an orthorhombic crystal; the orientation relationship is

Table 4. Structural Data for Joaquinite.

The unit cell axes *a* and *b* have been interchanged in columns 1-4 in order to agree with the definition of axes for this work.

	1	2	3	4	5	6	7
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space Group		*Ccmm* most probable	*Ccmm* most probable	*Ccmm* most probable	*C 2/m*	*Cc2m* *Ccm2* or *Ccmm*	*C2* *Cm*, or *C 2/m*
a	10.45Å	10.465Å	10.553Å	10.539(10)Å	10.52Å	10.48(2)Å	10.51(2)Å
b	9.61Å	9.616Å	9.699Å	9.680(5)Å	9.70Å	9.66(2)Å	9.66(2)Å
c	22.4Å	22.18Å	22.33Å	22.345(10)Å	11.83Å	22.26(2)Å	11.82(2)Å
β					109.7°		109.5(2)Å

1. San Benito County, California. Palache and Foshag (1932).
2. San Benito County, California. Bell (1963).
3. Seal Lake, Labrador. Bell (1963).
4. South Greenland. Semenov, *et al.* (1967).
5. San Benito County, California. J. F. Rowland (written communication from E. H. Nickel, 1970).
6. D6794, San Benito County, California. Precession films.
7. D6794, San Benito County, California. Precession and Weissenberg films.

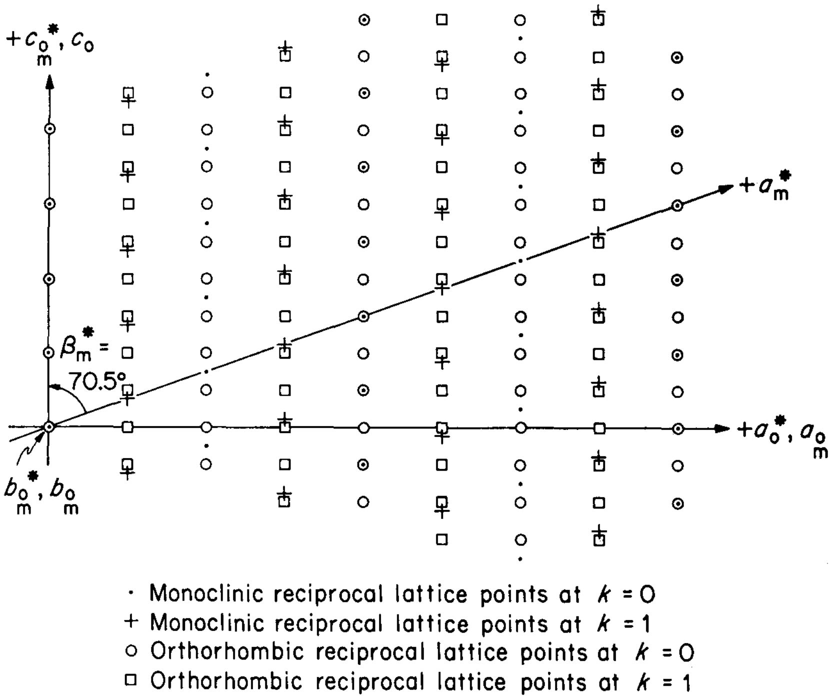

FIG. 4. Relationship between the orthorhombic (o) and monoclinic (m) reciprocal lattices of joaquinite. Reciprocal axes are shown by the symbol *.

the same as that shown in Figure 4. Similarly, the orthorhombic crystal shows a few very faint, but sharp reflections that correspond to a monoclinic crystal and its twin across (001). Therefore, although crystals of joaquinite appear to be simple on a macroscopic scale, they are composites of orthorhombic and monoclinic components at the X-ray diffraction level.

Electron beam scans were done with the microprobe on sample D6794 of joaquinite in order to determine if a difference in composition corresponding to the monoclinic-orthorhombic component boundaries could be seen. There is no compositional variation in Ba, Sr, Ce, Na, Fe, Mg, or Ti at a magnification of 5,000 and a spot size of ~1 μm. The two phases either must have identical compositions, and hence be polymorphs, or else the structural domains must be too fine to be resolved with the electron beam scans.

Using a density of 3.98 gm/cc, we computed the cation formula proportions for our monoclinic and orthorhombic cells. With the monoclinic cell, the number of Si cations for all analyzed points is 16.0(4);

the orthorhombic parameters give 32.0(7) for the number of Si cations for all analyzed points. Figure 5 shows the cation formula proportions for each analyzed point of joaquinite calculated by normalizing the formula proportions to Si = 32. Part of the scatter in the joaquinite analyses is due to measurement error, but much of this scatter represents inhomogeneity. Although joaquinite is more complicated than benitoite or neptunite, all three minerals were analyzed in the same microprobe runs; and the precision for joaquinite should not be much less than that for neptunite and benitoite (compare Figures 1 and 2 with 5).

The complete formula of joaquinite cannot be directly determined without knowing the Fe^{3+}, Li, and (OH) contents. However, a number of lines of evidence suggest that joaquinite is basically a sorosilicate, $A_2Si_2O_7$.

Joaquinite from sample D6794 is homogeneous and representative of all the analyses. Table 5 gives the formula proportions with Si normalized to 32 for this sample. Several features are present in these analyses:

a) The total number of cations other than Si (31.18) is nearly equal to that of Si. Figure 5 suggests that the variation in the total Fe + Mg + Mn may be partially matched by the range in Ti content but appears unrelated to changes in other analyzed elements. Li has an ionic radius similar to Fe, Mg, and Mn and may account for some of the Fe + Mg + Mn variation; a range in Li_2O content from zero to 0.55 weight percent (0 to 2 formula proportions of Li) will match the Fe + Mg + Mn variation. With the presence of Li, then, the total number of cations, excluding Si, equals the total number of Si cations.

b) The total positive charge ranges from 209 to 214 for all the analyzed points, with an average value of 210. In a simple anhydrous silicate this charge requirement is most closely met by a sorosilicate, basically $16(C_2^{3+}Si_2O_7)$; $A_2^{+}Si_2O_5$, $B_2^{2+}Si_2O_6$, and $D_2^{4+}Si_2O_8$ do not fit.

c) The small variation in the formula proportion of Ba about the value of 8 in Figure 5 suggests that Ba occupies a distinct position in the joaquinite structure. The formula proportion of Ti varies more than that of Ba, but it too approaches 8, suggesting a distinct position for Ti. The cations in Table 5 are ordered by their atomic radii. Ba is probably in eight-fold coordination and Ti in six-fold coordination. The rare earth elements plus Sr total about eight and may occupy an eight-fold coordinated position. The remaining cations, except Si and K, total about eight and may

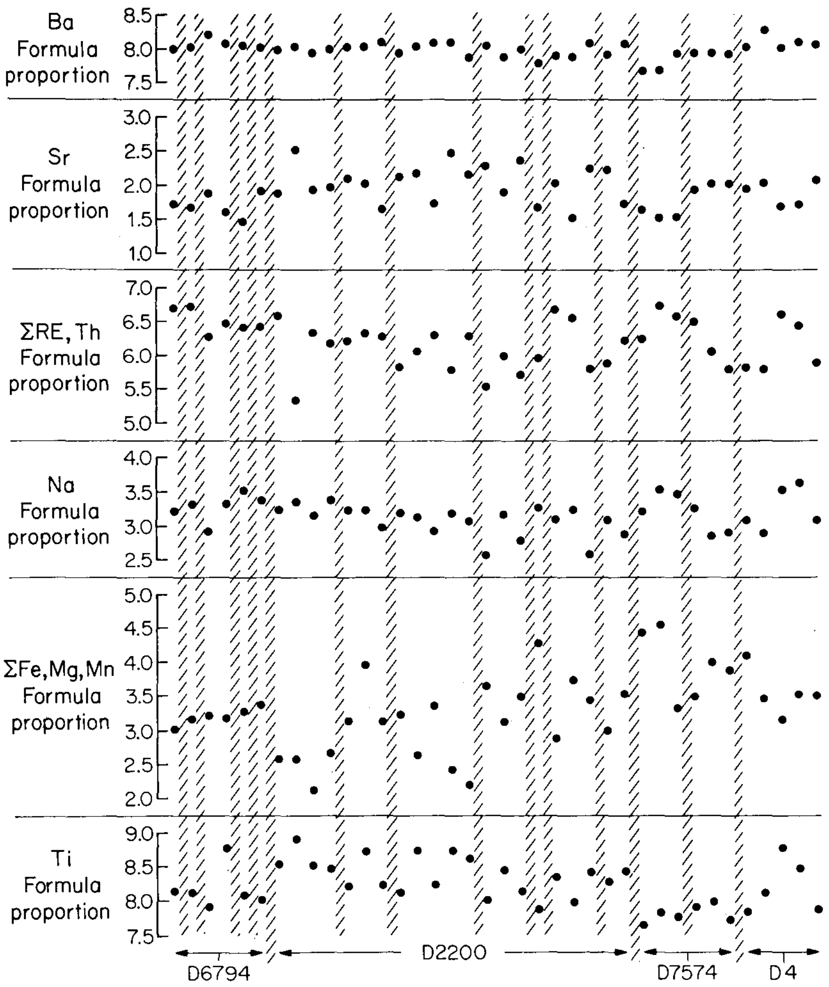

FIG. 5. Scatter diagram for the cation formula proportions of joaquinite samples from San Benito County, California. Each point represents a complete microprobe analysis, and analyses for each grain are grouped on the figure. Formula proportions are determined by normalizing the analyses to $\mathrm{Si} = 32$.

occur in six-fold coordination. Hence, a possible generalized distribution is

$$\mathrm{Ba}_{\sim 8}^{\mathrm{VIII}}\ (\mathrm{Sr}, RE)_{\sim 8}^{\mathrm{VIII}}\ (\mathrm{Ca, Na, Fe, Li, Mg})_{\sim 8}^{\mathrm{VI}}\ \mathrm{Ti}_{\sim 8}^{\mathrm{VI}}\ \mathrm{Si}_{32}^{\mathrm{IV}}$$

with possible coordination indicated by superscripts.

d) Since the actual mineral contains univalent, divalent, trivalent,

Table 5. Joaquinite formula proportions for the averaged analysis of D6794 and probable end members.

	Ionic Radii	Formula Proportion	
Ba^{+2}	1.34	8.05	
K^{+}	1.33	0.04	
Sr^{+2}	1.12	1.70	
La^{+3}	1.14	0.72	6.53
Ce^{+3}	1.07	3.58	
Pr^{+3}	1.06	0.42	
Nd^{+3}	1.04	1.05	
Th^{+4}	1.02	0.06	
Sm^{+3}	1.00	0.22	
Gd^{+3}	0.97	0.08	
Dy^{+3}	0.92	0.06	
Y^{+3}	0.92	0.34	
Ca^{+2}	0.99	0.20	
Na^{+}	0.97	3.32	
Fe^{+2}	0.74	3.13	
Li^{+}	0.68	(0.82)[a]	
Ti^{+4}	0.68	8.14	
Mg^{+2}	0.66	0.07	
Si^{+4}	0.42	32.00	

	Total Formula Proportions	
A^{+}	4.18	32.00
B^{+2}	13.15	
C^{+3}	6.47	
D^{+4}	8.20	
Si^{+4}	32.00	

Σ Cations = 64.00

Σ Cation charges = 210.7

(OH) = 11.5

O = 99.6

---

[a] Calculated by assigning the difference in total cations (except Li) from 64.00 to Li.

Proportions of possible formula end members

	A^{+}	B^{+2}	C^{+3}	D^{+4}	Si^{+4}	O	(OH)
4.18 $[AC(Si_2O_5)(OH)_2]$	4.18		4.18		8.36	20.90	8.36
2.29 $[BC(Si_2O_6)(OH)]$		2.29	2.29		4.58	13.74	2.29
8.20 $[BD(Si_2O_7)]$		8.20		8.20	16.40	57.40	
1.33 $[B_2(Si_2O_5)(OH)_2]$		2.66			2.66	6.65	2.66
	4.18	13.15	6.47	8.20	32.00	98.69	13.31

quadrivalent, and (OH) ions, there must be a number of coupled substitutions which can be expressed as theoretical end members. A generalized hydrous sorosilicate may be written as

$$(A^{+}, B^{2+}, C^{3+}, D^{4+})_2^{\text{charge}-6-x}\ Si_2O_{7-x}(OH)_x.$$

Possible substitutions are:

$$\begin{array}{lll} C_2^{3+}(\mathrm{Si_2O_7}) & A^{+}D^{4+}(\mathrm{Si_2O_6})(\mathrm{OH}) & A^{+}C^{3+}(\mathrm{Si_2O_5})(\mathrm{OH})_2 \\ B^{2+}D^{4+}(\mathrm{Si_2O_7}) & B^{2+}C^{3+}(\mathrm{Si_2O_6})(\mathrm{OH}) & A^{+}B^{2+}(\mathrm{Si_2O_4})(\mathrm{OH})_3 \\ & B_2^{2+}(\mathrm{Si_2O_5})(\mathrm{OH})_2 & A_2^{+}(\mathrm{Si_2O_3})(\mathrm{OH})_4 \end{array}$$

The analysis may then be expressed (see Table 5)

$$4.18\,[AC(\mathrm{Si_2O_5})(\mathrm{OH})_2] + 2.29\,[BC(\mathrm{Si_2O_6})(\mathrm{OH})] + 8.20\,[BD(\mathrm{Si_2O_7})] + 1.33\,[B_2(\mathrm{Si_2O_5})(\mathrm{OH})_2]$$

or

$$[(\mathrm{K_{0.04}Na_{3.32}Li_{0.82}})_{\Sigma=4.18}\,(\mathrm{Ba_{8.05}Sr_{1.70}Ca_{0.20}Fe_{3.13}Mg_{0.07}})_{\Sigma=13.15}\,(RE)_{6.47}(\mathrm{Th_{0.06}Ti_{8.14}})_{\Sigma=8.20}]_{\Sigma=32.00}\mathrm{Si_{32}O_{98.7}(OH)_{13.3}}.$$

This solution is not unique; other combinations of end members are possible.

Support for the suggestion that joaquinite is a sorosilicate is provided by the following observation: The O and OH formula proportions determined by reducing the chemical analysis to a number of possible coupled substitutions are close to those determined by assuming that the total number of cations is 64.00 and by assigning the deficiency in the analytic total from 100 percent to H_2O (98.7 *vs.* 99.6 and 13.3 *vs.* 11.5, respectively).

We suggest, then, that a general formula for joaquinite is

$$16\,\{[(A^{+}, B^{2+}, C^{3+}, D^{4+})_1^{\mathrm{VIII}}(A^{+}, B^{2+}, D^{4+})_1^{\mathrm{VI}}]^{\mathrm{charge}=6-x}\,\mathrm{Si}_2^{\mathrm{IV}}\mathrm{O}_{7-x}(\mathrm{OH})_x\}$$

and that the basic unit contains two eight-fold coordinated and two six-fold coordinated positions. The formula for the California occurrence of joaquinite is then

$$[\mathrm{Ba}_{8.1}^{\mathrm{VIII}}\,(\mathrm{Sr}_{1.7}RE_{6.5}\mathrm{Th}_{0.1})_{\Sigma=8.3}^{\mathrm{VIII}}\,(\mathrm{Ca_{0.2}Na_{3.3}Fe_{3.1}Li_{0.8}Mg_{0.1}})_{\Sigma=7.5}^{\mathrm{VI}}\cdot\mathrm{Ti}_{8.1}^{\mathrm{VI}}]_{\Sigma=32.0}\,\mathrm{Si}_{32.0}^{\mathrm{IV}}\mathrm{O}_{98.7}(\mathrm{OH})_{13.3}.$$

Semenov *et al.* (1967) reported the formula $NaBa_2Fe^{2+}Ce_2Ti_2Si_8O_{26}(OH)$ for joaquinite from southern Greenland which they said might be expressed as $(Na, Ba, Ce, Fe, Ti)_8Si_8O_{25}(OH, F)_3 = A_2Si_2O_7$. In addition, a number of structures have recently been refined for synthetic rare earth sorosilicates ($(RE)_2Si_2O_7$) by Smolin and Shepelev (1970).

Further single-crystal X-ray diffraction work is necessary, however, to determine an exact structural formula for joaquinite.

ACKNOWLEDGMENTS

Prof. George Rossman ran and interpreted the infrared spectrum of joaquinite. The Caltech microprobe is maintained in excellent operating condition by Mr. Arthur A. Chodos; his patience in discussing the efficient operation of the microprobe is greatly appreciated. We are indebted to Prof. Barclay Kamb and Mr. Rex Gibbons who gave generously of their time in helping to do and interpret the X-ray diffraction work. We thank Prof. J. H. Sturdivant, Dr. S. Samson, and Prof. Kamb for the use of their X-ray diffraction equipment. J. W. Adams and William N. Sharp provided standards for the *RE* analyses. Profs. W. A. Dollase, Kamb, and Rossman critically reviewed the manuscript. This investigation was supported by NSF grant (GA-12867). The microprobe laboratory has been developed with the support of the National Science Foundation, the Jet Propulsion Laboratory, and the Union Pacific Foundation.

REFERENCES

ALBEE, A. L., AND L. RAY (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates. *Anal. Chem.* 42, 1408–1414.

BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Oxidation state of iron in neptunite from Mössbauer spectroscopy. *Acta Crystallogr.* 22, 934–935.

BELL, K. W. (1963) X-ray diffraction examination of a Canadian occurrance of joaquinite. *Dept. Mines Tech. Surv., Geol. Surv. Can. Mineral. Sci. Internat. Rep.* MS-63-87.

BENCE, A. E., AND A. L. ALBEE (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* 76, 382–403.

BERRY, L. G. (1963) Neptunite: Unit cell and X-ray powder data. *Can. Mineral.* 7, 679–681.

BRADLEY, W. M. (1909) On the analysis of the mineral neptunite from San Benito County, California. *Amer. J. Sci.* 28, 15–16.

CANNILLO, E., F. MAZZI, AND G. ROSSI (1966) The crystal structure of neptunite. *Acta Crystallogr.* 21, 200–208.

FISCHER, K. (1969) Verfeinerung der Kristallstruktur von Benitoit $BaTi(Si_3O_9)$. *Z. Kristallogr.* 129, 222–243.

HEINRICH, E. W., AND S. H. QUON (1963) Neptunite from Seal Lake, Labrador. *Can. Mineral.* 7, 650–654.

LARSEN, E. S., AND H. BERMAN (1934) The microscopic determination of the nonopaque minerals. *U. S. Geol. Surv. Bull.* 848, 127.

LOUDERBACK, G. D., AND W. C. BLASDALE (1909) Benitoite, its paragenesis and mode of occurrence. *Univ. Calif. Dept. Geol. Bull.* 5, 331–380.

MURDOCH, J., AND R. W. WEBB (1948) Minerals of California. *Calif. Div. Mines Bull.* 136, 222.

PALACHE, C., AND W. F. FOSHAG (1932) The chemical nature of joaquinite. *Amer. Mineral.* 17, 308–312.

SEMENOV, E. I., V. I. BUKIN, Y. A. BALASHOV, AND H. SØRENSEN (1967) Rare earths in minerals of the joaquinite group. *Amer. Mineral.* 52, 1762–1769.

SMOLIN, Y. I., AND Y. F. SHEPELEV (1970) The crystal structures of the rare earth pyrosilicates. *Acta Crystallogr.* B26, 484–492.

ZACHARIASEN, W. H. (1930) The crystal structure of benitoite, $BaTiSi_3O_9$. *Z. Kristallogr.* 74, 139–146.

Manuscript received, April 1, 1971; accepted for publication, August 23, 1971.