Strontiojoaquinite and bario-orthojoaquinite: two new members of the joaquinite group

WILLIAM S. WISE

Department of Geological Sciences
University of California
Santa Barbara, California 93106

Abstract

Two new minerals have been found in San Benito County, California, that are structurally and chemically related to joaquinite. A combination of electron and ion microprobe analyses of strontiojoaquinite yields the formula $(Na_{2.28}Li_{0.11}Fe_{1.44}\square_{0.17})$ $\square_2Ba_4Ti_4[O_{1.27}(OH)_{2.73}]Sr_{4.01}REE_{0.01}[Si_4O_{12}]_4 \cdot 1.62H_2O$. The virtual absence of REE indicates that this is the Sr analog of joaquinite.

X-ray single crystal study showed the mineral to be monoclinic with the same submicroscopic twinning and one dimensional disorder exhibited by joaquinite. Several reflections in the X-ray powder pattern show that the space group must be $P2$, Pm, or $P2/m$, as compared to the $C2$ of joaquinite. Refined cell dimensions are a 10.516(6), b 9.764(5), c 11.87(1)Å, β 109°17(4)' $Z = 1$. The strongest lines in the X-ray powder pattern are 2.801(100)(004,311), 2.967(72)(023), 3.001(48)(113), 2.923(45)(301), 2.611(42)($\bar{4}$01,$\bar{4}$02), 2.432(40)(312), and 4.30(35)($\bar{1}$21).

The pseudo-orthorhombic, bipyramidal crystals have the forms {110}, {11$\bar{1}$}, and {001}. All crystals are zoned with a joaquinite core. Strontiojoaquinite is green, yellow-green, and less commonly yellow-brown. Hardness (Mohs) is 5½; cleavage {001}, good. Calculated density is 3.68 g/cm^3. It is optically biaxial, positive, 2V 35° to 45° with strong dispersion of the optic axes $r > v$. Refractive indices are α 1.710(2), β 1.718(2), γ 1.780(3). Optical orientation and axial colors: X (colorless):$a = 19°$, Y (colorless) $= b$, Z (yellow) $= c$; absorption $X = Y < Z$.

A combination of electron and ion microprobe analyses of bario-orthojoaquinite yields the formula $(Na_{0.10}Fe_{3.61}Mn_{0.24})\square_2Ba_4(Ti_{3.88}Al_{0.12})(Ba_{2.88}Sr_{0.88}Ca_{0.08}Al_{0.19})O_4[Si_4O_{12}] \cdot 2H_2O$. The absence of REE and the excess Ba indicates that this mineral is the Ba analog of joaquinite.

X-ray single crystal study showed it to be orthorhombic, space group $Ccmm$, $CC2m$, or $Ccm2_1$, a 10.477(5), b 9.599(1), c 22.59(1)Å, $Z = 2$. The strongest lines in the X-ray powder pattern are 2.997(100)(224), 2.953(95)(132), 2.824(90)(008), 5.64(70)(004), 2.935(70)(117), 4.30(62)(203), 3.203(50)(223), and 2.602(50)(401). Crystals are up to 8 mm in diameter, in the form of steep bipyramids {111} truncated by the basal pinacoid, and are yellow-brown with a vitreous luster. Hardness (Mohs) is 5½. Cleavage {001}, good. Measured density is 3.959(2) g/cm^3 (calculated, 3.962 g/cm^3). It is optically biaxial, positive, 2V 10° to 15°, with strong dispersion of the optic axes $r > v$. Refractive indices are α 1.735(2), β 1.737(2), γ 1.80(1). Optic orientation and axial colors: X(very pale yellow) $= a$, Y (pale yellow) $= b$, and Z (yellow) $= c$, absorption $X < Y << Z$.

These two new minerals, along with others previously described, allow names of the joaquinite group minerals to be based on the symmetry and occupancy of the REE position: REE-bearing members are joaquinite and orthojoaquinite; Sr-bearing, strontiojoaquinite and strontio-orthojoaquinite; and Ba-bearing, bario-orthojoaquinite.

Introduction

The characterization of the mineral joaquinite was not complete for nearly 70 years following its initial discovery and naming (Louderback, 1909). The type locality is the well known Benitoite Gem Mine in San Benito County, California. X-ray and morphological studies by Palache and Foshag

(1932) suggested that the mineral had orthorhombic symmetry, and their chemical analysis yielded the formula $NaBa(Ti,Fe)_3Si_4O_{15}$. There was little further work on the mineral until two new occurrences, Seal Lake, Quebec (Bell, 1963) and Ilimaussaq, Greenland (Semenov et al., 1967) lead to renewed interest in the mineral. Semenov and his co-workers found that the rare earth elements (REE) are an essential part of the composition of joaquinite from all three localities. Laird and Albee (1972) conducted a thorough study of the X-ray properties and the composition of a number of crystals from the type locality. This work, not only further defined the composition, but also demonstrated that the crystals are monoclinic, although parts of a few were found to be orthorhombic. Furthermore, Laird and Albee found that the orthorhombic-appearing crystals exhibit submicroscopic, polysynthetic twinning parallel to {001}.

The crystal structure of joaquinite was studied by Cannillo et al. (1972) on relatively untwinned material from Greenland. Although they based their analysis on the monoclinic space group $C2/m$ and did not detect several atoms, the basic structure did emerge. This structure was refined by Dowty (1975) using the space group $C2$, and the positions for the remaining atoms were located.

Semenov et al. (1967) and Laird and Albee (1972) found such variation in the composition of the crystals they analyzed, that they proposed a number of possible end members and referred to the whole as the joaquinite group. Recent collecting in San Benito County has lead to the discovery of two members of the group, one in which the REE have been replaced by Sr and the other by Ba. The compositional adjustments to maintain charge balance in these phases provides a further understanding of the composition and symmetries of the group. This paper describes these new minerals, fits their compositions into a general scheme, and proposes a system of nomenclature for the group. The new minerals, mineral names, and group nomenclature have been approved by the I.M.A. Commission for New Minerals and Mineral Names.

The joaquinite group

Based on his structure refinement Dowty (1975) proposed an ideal formula for joaquinite, $Na_2Fe_2^{2+}(OH)_2Ba_4Ti_4O_4REE_4[Si_4O_{12}]_4\cdot2H_2O$. The structure is characterized by Si_4O_{12} rings (see Cannillo et al., 1972, and Dowty, 1975), connected by Ti ions. These bonded rings form sheets parallel to

(001), which gives rise to a pseudotetragonal morphology and the basal cleavage. The Ti-bonded Si_4O_{12} sheets are held together in two ways, one by a sheet of Ba and O ions and water molecules, and the other by Na, Fe^{2+}, OH, and the ions of the REE position. The Na, Fe, and OH occur along 2-fold axes and have a multiplicity of only 2. There is one site preferred by Na and another by Fe^{2+} (Dowty, 1975, Fig. 2), but in most joaquinites these positions and the OH position are not completely filled. In the minerals described here Na and Fe substitute for each other, and more importantly the REE ions are completely replaced by divalent ions such as Sr and Ba.

Group composition

A number of joaquinite group crystals were analyzed as part of this study, and a selection of analyses is presented in Table 1. All samples were analyzed for the major elements with an electron microprobe. Crystals or groups of crystals (about 1 mm in diameter) were embedded in epoxy and ground to expose the center of the crystals. Such grains were analyzed in at least four spots to determine the extent (if any) of compositional zoning.

Standards used were benitoite (Ba, Ti, and Si), hematite (Fe), rhodonite (Mn), celestite (Sr), albite (Na and Al), andesine (Ca), and synthetic rare earth glasses (Drake and Weill, 1972). The analyses were carried out under the following conditions: accelerating voltage 15 kV for all elements, sample current 8 nA, and a spot diameter 10 to 20 μm. Emission data were reduced and interelement corrections applied with a modified version of EMPADR 7 (Rucklidge and Gasparrini, 1969).

Because two samples represented new compositions for the joaquinite group, mass scans with an ARL ion probe were performed. The ion probe microanalyses were carried out with a negatively charged primary beam of monatomic $^{16}O^-$ at 17 kV. The spot size was approximately 20 μm and a sample current of 6 nA. The hydrogen content was estimated from the working curves of Hinthorne and Anderson (1975), and other element data were quantitatively reduced, using sensitivity factors derived from a theoretical ionization model (Anderson and Hinthorne, 1973).

Combined results of both microprobe methods are presented in Table 1. The ideal formula for joaquinite has an anionic charge of -106. If the number of cations in the analyses of Table 1 are

Table 1. Microprobe analyses and cell contents of various members of the joaquinite group from San Benito County, California

	1	2	3	4	5	6	7
SiO$_2$	37.54	35.87	37.57	34.99	35.15	36.16	34.75
TiO$_2$	12.48	12.86	12.45	12.01	11.33	12.54	10.95
Al$_2$O$_3$	0	0	0	0	.57	.16	.24
FeO	4.03	3.91	5.04	3.96	9.47	3.13	3.23
MnO	0	.14	0	.09	.62	.09	.41†
BaO	24.52	23.22	26.39	22.51	38.56	23.81	22.40
SrO	16.23	8.37	12.45	4.07	3.34	4.91	.31
CaO	0	0	0	0	.17	0	0
Na$_2$O	2.76	2.01	2.60	1.99	.12	2.02	2.45
Li$_2$O	.03*	.12*	nd	nd	0 *	nd	nd
Y$_2$O$_3$	0	0	0	0	0	.12	.73
La$_2$O$_3$	.14*	1.43	0	4.89	0	2.31	5.62
Ce$_2$O$_3$	.003*	4.56	.27	7.99	0	9.17	9.89
Pr$_2$O$_3$	.003*	.82	0	1.03	0	.38	.94
Nd$_2$O$_3$	.05*	2.88	0	1.91	0	1.91	3.85
Sm$_2$O$_3$	0	0	0	.29	0	.22	.67
Gd$_2$O$_3$	0	.65	0	1.14	0	1.09	1.47
Dy$_2$O$_3$	0	.45	0	.39	0	.33	.49
H$_2$O	2.1*	nd	nd	nd	1.3	nd	nd
	99.85	97.29	98.05	97.26	100.63	98.34	98.38
Cell Contents							
Si	16.00	16.00	16.00	16.00	16.00	16.00	16.00
Ti	4.00	4.32	3.99	4.13	3.88	4.17	3.79
Ba	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Fe	1.44	1.46	1.80	1.51	3.61	1.16	1.24
Mn	0	.05	0	.03	.24	.03	.23†
Na	2.28	1.74	2.15	1.76	.10	1.73	2.18
Li	.11	.47	–	–	0	–	–
Ba	.09	.06	.40	.03	2.88	.13	.04
Sr	4.01	2.16	3.39	1.08	.88	1.26	.08
Ca	0	0	0	0	.08	0	0
Al	0	0	0	0	.31	.09	.13
Y	0	0	0	0	0	.03	.18
X La	.0105	.24	0	.82	0	.38	.96
Ce	.0002	.74	.04	1.34	0	1.49	1.66
Pr	.0002	.13	0	.17	0	.06	.16
Nd	.0036	.46	0	.31	0	.30	.64
Sm	0	.05	0	.05	0	.03	.10
Gd	0	.10	0	.17	0	.16	.22
Dy	0	.06	0	.06	0	.05	.07
OH	2.73	–	–	–	0	–	–
H$_2$O	1.62	–	–	–	1.87	–	–
Σch	101.51	104.29	101.41	104.34	103.93	103.34	104.88
Σ X	4.11	4.00	3.83	4.03	4.04#	3.91	3.99#

0 for a reported content means that element was below the detection limit for the electron microprobe

nd and – indicate that the element was not determined

* element abundance was determined by ion microprobe

† these values include 0.26 wt % MgO and 0.17 Mg in the cell contents

Σ X is the total of all cations assigned to the X position

Al has been partitioned between the Ti position and X to fill each

Σch is the total cationic charge based on 16 Si

1. Strontiojoaquinite, yellow-green outer margin of a crystal from Mina Numero Uno, 2.0 miles west of San Benito Mountain, San Benito County, California.

2. Joaquinite core of the same crystal as in column 1.

3. Strontiojoaquinite outer margin of a crystal from the locality 2 miles southwest of San Benito Mountain, San Benito County, California.

4. Joaquinite core of the same crystal as in column 3.

5. Bario-orthojoaquinite from the Benitoite Gem Mine, San Benito County, California.

6. Joaquinite from the Benitoite Gem Mine.

7. Joaquinite, Santa Rita Peak, one mile north of the Benitoite Gem Mine.

proportioned to this charge all but one yield amounts of Si greater than 16. Because the four Si$_4$O$_{12}$ rings seem to be the most tightly constrained feature of the joaquinite structure, it appears likely

that the total anionic charge may be somewhat variable. Therefore, the unit cell contents were proportioned by setting the number of Si to 16. The total cationic charge, the number of Ti ions, and the total number of ions in the X position can be used to check the quality of the analysis. If the oxygen ions between the Si$_4$O$_{16}$ rings can be replaced by OH, and if the hydroxyl sites on the Na and Fe 2-fold axes (Dowty, 1975, Fig. 2) can be vacant (see evidence below), then the cation charge can be as low as +100. The maximum of +106 requires that all four bridging oxygens and both hydroxyls be present.

Table 1 contains analyses of joaquinite from three other localities in San Benito County, as well as one from the type locality (column 6). An examination of the cell contents reveals several features of the site filling in the joaquinite structure. For example, the analyses show an irregular filling of the Ti site. Those with an excess of 4.00 may reflect an accumulation of analytical errors. The two samples with a deficiency of Ti (columns 5 and 7) also contain the highest Al, which may be in the Ti site. This is especially likely in the case of sample 5 where there are no other +4 ions, such as Zr, Nb, or Th available. Even though there are other compositional variations, the most significant is the substitution of Sr and Ba into the REE site. All of these variations (Table 1) lead to a general formula for the joaquinite group: (Na,Fe^{2+})$_{4-x}$(OH)$_{2-y}$Ba$_4$Ti$_4$[O$_{4-z}$(OH)$_z$]X$_4$[Si$_4$O$_{12}$]$_4$·2H$_2$O, where X is REE, Sr, or Ba.

Symmetry and nomenclature

Because the X-ray work reported by Palache and Foshag (1932) suggested orthorhombic symmetry, the type joaquinite has long been assigned to that crystal system. Joaquinite crystals do have an orthorhombic morphology (see Wise and Gill, 1977, Fig. 26), but zero level {h0l} precession photographs demonstrate monoclinic symmetry (see Cannillo et al., 1972). Several crystals of joaquinite from the type specimen described by Palache and Foshag were examined on a precession camera, and all were found to be monoclinic with submicroscopic, polysynthetic twinning.

A system of nomenclature, presented in Table 2, is based on the crystal symmetry and on the composition of the X position. The name joaquinite is to be used for the mineral that is monoclinic and REE-rich, and orthojoaquinite for material found by Laird and Albee (1972) and Dowty (1975) that is

Table 2. Nomenclature for known members of the joaquinite group

Mineral name	Dominant ion in X	Crystal system	Space group	Cell dimensions (in Å)	Reference
joaquinite	REE	monoclinic	C2	$a = 10.516$, $b = 9.686$ $c = 11.833$, $\beta = 109.67°$	Dowty (1975)
orthojoaquinite	REE	orthorhombic	Ccmm, Ccm2₁, or Cc2m	$a = 10.48$, $b = 9.66$, $c = 22.26$	Dowty (1975)
strontiojoaquinite	Sr	monoclinic	P2, Pm, P2/m	$a = 10.516$, $b = 9.764$ $c = 11.87$ $\beta = 109°$ 17'	this paper
strontio-orthojoaquinite	Sr	orthorhombic	Pcam, Pca2₁	$a = 10.517$, $b = 9.777$ $c = 22.392$	Chihara et al (1974)
bario-orthojoaquinite	Ba	orthorhombic	Ccmm, Ccm2₁, Cc2m	$a = 10.477$, $b = 9.599$ $c = 22.59$	this paper

REE-rich but shown by X-ray diffraction to be orthorhombic.

It is in this framework that two new members of the joaquinite group are described.

Strontiojoaquinite

Strontiojoaquinite occurs in the same general area and geologic environment as the original joaquinite, but it is recognized as a new mineral by the replacement of the rare earth elements with Sr.

Occurrence

Strontiojoaquinite was first found by Sharon and Eugene Cisneros at a claim, named Mina Numero Uno, jointly mined with Carol and Gary Mathiason. The claim is located along the south side of Clear Creek 2.0 miles west of San Benito Mountain (New Idria quadrangle, 15' series), San Benito County, California. The claim is approximately 5 miles northwest of the Benitoite Gem Mine.

The mineral locality is in a large lens of metamorphosed basalt, included as a tectonic block within the New Idria serpentine body (see Coleman, 1957, and Wise and Gill, 1977). The basaltic block has been subjected not only to high pressure metamorphism, but to considerable compositional modification by fluids during the emplacement of the peridotite and serpentinization. The meta-basalt is composed of a fine-grained intergrowth of albite, crossite, and acmite. The rock mass was fractured during the emplacement, forming gashes and irregular open spaces commonly a few millimeters to a centimeter wide. The cavities are lined with recrystallized albite and crossite, and they contain irregular concentrations of small crystals of benitoite (about 5 mm) and neptunite and even rarer, smaller crystals (about 1 mm) of strontiojoaquinite.

The same mineral was found by A. L. McGuinness and Charles Trantham at a locality two miles southwest of San Benito Mountain. At this occurrence the strontiojoaquinite is associated with abundant albite and actinolite and sparse benitoite (up to 10 mm across), neptunite, analcime, and natrolite in veins cutting a tectonic block of meta-graywacke. The host rock is composed of a granular assemblage of albite, actinolite, and titanite with the relict sandstone texture weakly discernible.

Composition

Traverses across crystal sections with electron and ion microprobes demonstrate that crystals from both localities are zoned from REE-rich cores to Sr-rich rims. A typical crystal is 0.5 mm wide; the joaquinite core is about 0.2 mm across with a sharp transition to the lighter colored strontiojoaquinite overgrowths (Fig. 1). Table 1 lists analyses of the strontiojoaquinite rims (columns 1 and 3) and joaquinite cores (columns 2 and 4) for a crystal from each of the two localities. Major element concentrations were measured with the electron microprobe and for the Mina Numero Uno sample (column 1) complete mass scans were made to determine elements in low abundance, as well as those with low atomic number.

Several important aspects of the composition should be noted in comparison to the joaquinite cell contents. There is little variation in the occupancy of the Ba and Ti sites and apparently in the Si_4O_{12} rings. The sympathetic variation of Sr and REE clearly indicates the substitution of Sr into the REE site. Just as in various joaquinites there is variation in the occupancy of the Na and Fe sites.

In order to account for the charge balance with the anionic framework, there must be a different
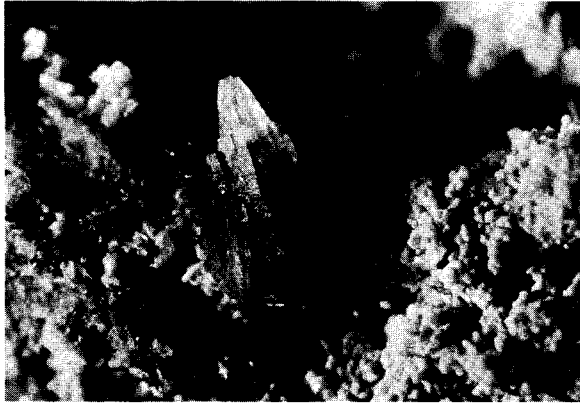
Fig. 1. Strontiojoaquinite from Mina Numero Uno, San Benito County, California. The crystal displays the typical bipyramidal form truncated by small basal faces. The dark joaquinite core colors the center of the crystal in contrast to the light upper portion. The crystals have grown on albite and crossite, partially covered with montmorillonitic clay on the right side. Total height of the crystal group is 2 mm.

pyramid faces (Fig. 1) are caused by alternations of the faces of the two major forms.

A cleavage fragment from the clear yellow-green end of a crystal was chosen for X-ray examination. Zero level precession photographs $\{hk0\}$ and $\{h0l\}$ showed the mineral to have the same crystallographic orientation and twinning as joaquinite. For example, the $\{h0l\}$ photograph shows the polysynthetic twinning that leads to pseudoorthorhombic symmetry with an 88.8Å c-dimension (Cannillo *et al.*, 1972). The two photographs provided trial values for cell refinement of X-ray powder data, standardized with Si metal ($a = 5.4309$Å), using CuKα X-radiation ($\lambda = 1.5418$Å). The indexed powder pattern is compared to that for joaquinite in Table 3.

Several reflections in the powder pattern show that the space group must be Pm, $P2$, or $P2/m$, as

distribution of the hydrogen from the ideal joaquinite structure. The following is a summary of the substitutions (Table 1, column 1):

$4\ Sr^{2+} \rightarrow 4\ REE^{3+}$ resulting in a -4.0 charge

$0.39\ (Na,Li)^+ \rightarrow Fe^{2+}$ resulting in a -0.34 charge

$0.17\ \square \rightarrow Fe^{2+}$ resulting in a -0.39 charge

$2.0\ \square \rightarrow 2(OH)^-$ resulting in a $+2.00$ charge

$2.73\ (OH)^- \rightarrow 2.73\ O^{2-}$ resulting in a $+2.73$ charge.

If this charge accounting and hydrogen redistribution is correct, the strontiojoaquinite from the type locality has the following empirical formula: $(Na_{2.28}Li_{0.11}Fe^{2+}_{1.44}\square_{0.17})\square_2Ba_{4.09}Ti_{4.00}\ [O_{1.27}(OH)_{2.73}]$ $Sr_{4.01}REE_{0.01}[Si_4O_{12}]_4 \cdot 1.62H_2O.$[1] There are not sufficient compositional data to determine the limits on the occupancy of the Na, Fe, OH, and O sites in strontiojoaquinite, therefore, the general formula should be written $(Na,Fe)BaTi(O,OH)Sr[Si_4O_{12}] \cdot$ $0.4H_2O$, (Z = 4).

Crystallography

Strontiojoaquinite occurs in the form of steep, pseudotetragonal bipyramidal crystals (Fig. 1). Steep faces are in the forms $\{11\bar{1}\}$ and $\{110\}$, and are truncated with a small basal face. Striations on the

[1]$\square_2$ Represents two vacant OH sites (y = 2).

Table 3. X-ray powder diffraction data for strontiojoaquinite and joaquinite

hkl	Strontiojoaquinite			Joaquinite		
	d_{calc}	d_{meas}	I/I_o	d_{calc}	d_{meas}	I/I_o
001	11.2	11.3	15	-	-	-
110	-	-	-	6.93⎫	6.94	13
1̄10	-	-	-	6.93⎭		
1̄11	-	-	-	6.62	6.61	6
002	5.60	5.61	20	5.57	5.57	45
1̄12	-	-	-	4.95	4.96	12
020	4.88	4.87	4	4.84	4.85	6
2̄02	-	-	-	4.54	4.54	38
021	4.48	4.47	40	4.44	4.44	64
1̄21 *	4.30	4.30	35	-	-	-
201	4.07	4.06	7	4.05	4.05	26
112	-	-	-	3.91	3.91	23
022	3.68	3.68	10	3.65	3.66	15
2̄21	3.57	3.55	7	3.55	3.56	15
220	-	-	-	3.46	3.47	5
3̄11	3.297	3.301	33	3.295	3.296	52
122 *	3.230	3.232	35	-	-	-
202	3.224	3.220	35	3.20	3.21	10
221	-	-	-	3.105	3.106	75
1̄23 *	3.072	3.079	24	-	-	-
130	-	-	-	3.071	3.068	40
113	3.013	3.011	48	2.990	2.991	42
023	2.966	2.967	72	2.946	2.946	90
301, *	2.922	2.923	45	-	-	-
3̄13	-	-	-	2.887	2.890	82
1̄14	-	-	-	2.823	2.825	30
004	2.801⎫	2.801	100	2.783⎫	2.784	100
311	2.799⎭			2.785⎭		
320 *	2.739	2.736	20	-	-	-
222	-	-	-	2.671	2.675	6
4̄01	2.612⎫	2.611	42	2.611⎫	2.611	45
4̄02	2.610⎭			2.613⎭		
203	-	-	-	2.581	2.581	25
3̄14	2.516	2.518	5	2.515	2.515	12
2̄24	2.481⎫	2.475	12	2.473	2.471	5
4̄03	2.478⎭					
312	2.430	2.432	40	2.415	2.416	50
041	2.385	2.386	15	2.367	2.368	5
401	2.270	2.268	28	2.261	2.260	32
042	2.238	2.238	25	2.221	2.219	15

* *Indices of these peaks indicate that strontiojoaquinite has a P-cell compared to the C-cell of joaquinite.*

compared to $C2$ of joaquinite (Dowty, 1975). The refined cell dimensions are $a = 10.516(6)$, $b = 9.764(5)$, $c = 11.87(1)$Å, and $\beta = 109°17(4)'$.

Physical properties

Strontiojoaquinite is green, yellow-green, and less commonly yellow-brown. The joaquinite core is commonly visible, causing a dark brown center of the crystal (Fig. 1). Hardness (Mohs) is 5½; cleavage is good and parallel to {001}. Because the crystals are all zoned, the density was not measured, but the calculated density from the empirical formula is 3.68 g/cm^3.

Optically strontiojoaquinite is biaxial positive with 2V varying from 35° to 45° with strong dispersion of the optic axes, $r > v$. Refractive indices are $\alpha = 1.710(2)$, $\beta = 1.718(2)$, and $\gamma = 1.780(3)$. The optic plane is parallel to {010} with $Y = b$, $Z = c$, and $X:a = 19°$. The crystals are weakly pleochroic with $X = Y$ (colorless) $< Z$ (yellow).

Name and type specimen

The name is based on the dominant ion in the X position and on the monoclinic symmetry. Type material has been deposited in the mineral collection at the University of California, Santa Barbara, and cotype specimens in the U.S. National Museum, Washington, D.C. and the Harvard Mineralogical Museum, Cambridge, Massachusetts.

Bario-orthojoaquinite

Bario-orthojoaquinite was found in a single block (approximately 0.5 m on a side) of altered meta-basalt at the Benitoite Gem Mine in San Benito County, California. The occurrence is very similar to that of the original joaquinite, but the crystals are several times larger. The mineral was recognized as a new member of the joaquinite group by its orthorhombic symmetry and extra high content of barium.

Occurrence

In 1978 the current leasees (E. Gray and W. Forrest) of the Benitoite Gem Mine deepened the small pit that currently constitutes the mine (Wise and Gill, 1977). Most of the excavated blocks were crossite-bearing meta-basalt, cross-cut by natrolite-filled veins barren of any of the well known benitoite, neptunite, and joaquinite. However, one block, found by Robert Gill and me, contains colorless benitoite and large (up to 8 mm) crystals having the appearance of joaquinite.

The host rock, typical of the Benitoite Gem Mine, is a highly fractured meta-basalt composed of albite, crossite, actinolite, and acmite. Sparse crystals of bario-orthojoaquinite (from 2 to 8 mm) are associated with colorless plates of benitoite (up to 10 mm across), partially replaced by baotite and fresnoite. Late fluids leached the host rock of albite and acmite within a few millimeters of the fracture surface, partially dissolved the bases of bario-orthojoaquinite crystals, apparently caused the conversion of benitoite to baotite and fresnoite, and filled the fractures with massive natrolite.

Composition

The compositions of the bario-orthojoaquinite crystals are remarkably uniform, especially in view of their large size. A complete analysis of one such crystal is given in Table 1, column 5. It is useful to compare this analysis with that of a typical joaquinite crystal (column 6). Analyses of several spots on several crystals reveal a uniformity in composition, but there are some unusual features. Most important is the extra large amount of Ba, which obviously cannot be accommodated in the regular Ba site, and the complete absence (at least below detection limits) of rare earth elements. Furthermore, there is a high content of iron and a correspondingly low content of Na. Ti is slightly low, but is accompanied by a minor, persistent Al content near 0.50%.

These compositional variations require a careful review of the charge balance, which within the limits of the analytical error can be summarized as follows:

3.84 $(Ba,Sr,Ca)^{2+}$	resulting in a
$\rightarrow 3.84$ REE^{3+}	-3.84 charge
1.85 $(Fe,Mn)^{2+}$	resulting in a
$\rightarrow 1.85$ Na^+	$+1.85$ charge
0.05 $\square \rightarrow 0.05$ Na^+	resulting in a
	-0.05 charge
0.12 Al^{3+}	resulting in a
$\rightarrow 0.12$ Ti^{4+}	-0.12 charge
2.0 $\square \rightarrow 2.0$ $(OH)^-$	resulting in a
	$+2.00$ charge

These substitutions essentially balance the anionic charge, indicating that Fe^{2+} fills the Fe and much of the Na sites and that Al fills the remaining X position sites. If these substitutions are correct, the bario-orthojoaquinite has the following empirical formula: $(Na_{0.11}Fe_{3.61}Mn_{0.24}\square_{0.05})\square_2Ba_4(Ti_{3.88}Al_{0.12})$

Fig. 2. Bario-orthojoaquinite from the Benitoite Gem Mine, San Benito, California. The crystal displays the typical striated and curved bipyramid faces, and is embedded in massive natrolite. Height of exposed crystal is 7 mm.

$(Ba_{2.88}Sr_{0.88}Ca_{0.08}Al_{0.19})O_4[Si_4O_{12}]_4 \cdot 2.0H_2O$. A general formula for bario-orthojoaquinite can be written as $Fe_4^{2+}Ba_4Ti_4(Ba,Sr)_4O_4[Si_4O_{12}]_4 \cdot 2H_2O$, (Z = 2).

Crystallography

Bario-orthojoaquinite occurs in the form of truncated, pseudotetragonal bipyramids (Fig. 2). Steep faces are the form {111} with a basal {001} termination. The pyramidal faces are striated and curved (convex) resulting in a concave curved c-face. The striations are from alternating (111) and (11$\bar{1}$) faces.

Cleavage fragments were examined by precession and Weissenberg photographs to determine the cell dimensions and space group symmetry. The zero level {h0l} precession photograph ruled out monoclinic symmetry typical of joaquinite. Zero, first, second, and third level Weissenberg photographs (0kl, 1kl, 2kl, and 3kl) were taken to check for proper indexing and systematic extinctions. The cell dimensions were refined from the X-ray powder pattern (Table 4), standardized with Si metal (a = 5.4309Å), using CuKα X-radiation (λ = 1.5418Å).

The diffraction symmetry is mmm affirming orthorhombic symmetry. Indexing of the Weissenberg photographs is limited to h + k = 2n in hkl reflections and l = 2n in 0kl reflections, which lead to the space groups Ccmm, Ccm2₁, or Cc2m. The cell dimensions are a = 10.477(5), b = 9.599(1), and c = 22.59(1)Å.

Physical properties

Bario-orthojoaquinite is yellow-brown with a vitreous luster and a pale yellow streak. The density

was measured on several fragments (10 to 15 mg) with a Berman balance, using toluene as an immersion liquid. The measured value of 3.959(2) g/cm³ compares well to the calculated 3.962 g/cm³.

The crystals commonly show strain lamellae parallel to (001). Optically unstrained portions are biaxial positive with 2V varying between 10° and 15° and strong dispersion of the optic axes r > v. The optic plane is parallel to (010), X = a and Z = c. Refractive indices are α = 1.735(2), β = 1.737(2), and λ = 1.80(1). Crystals exhibit distinct pleochro-

Table 4. X-ray powder data for bario-orthojoaquinite

hkℓ	d_{calc}	d_{meas}	I/I_o
110	7.08	7.14	5
111	6.75	6.76	11
112	6.00	6.02	5
004	5.65	5.64	70
201	5.10	5.11	12
202	4.75	4.74	14
022	4.417	4.418	38
203	4.300	4.303	62
204	3.840	3.834	17
024	3.65	3.66	8
220	3.54	3.56	11
221	3.50	3.52	14
205	3.421	3.424	12
310	3.282	3.286	37
311	3.284	3.25	23
223	3.203	3.203	50
312	3.151	3.153	12
130	3.060	3.063	28
131	3.033	3.028	45
224	2.999	2.997	100
132	2.954	2.953	95
117	2.936	2.935	70
008	2.824	2.824	90
225	2.786	2.78	23
207	2.748	2.750	38
400	2.619	2.62	15
401	2.602	2.602	50
402	2.551	2.551·	12
316	2.474	2.48	14
–	–	2.455	18
028	2.434	2.424	15
136	2.375	2.373	15
333	2.309	2.311	9
405	2.266	2.264	32
422	2.252	2.254	26
044	2.209	2.211	18
423	2.199	2.201	15
242	2.142	2.144	18
0 2 10	2.044	2.045	22
1 1 11	1.972⎫	1.969	16
245	1.965⎭		
2 0 11	1.912	1.913	25
151	1.882	1.882	17
427	1.872	1.870	15
048	1.829	1.828	9
409	1.812	1.812	18

+9 peaks to 1.54

ism: X (very pale yellow), Y (pale yellow), and Z (yellow) with $X < Y << Z$.

Name and type specimen

The name is based on the dominant ion in the X position and on the orthorhombic symmetry (Table 2). Type material has been deposited in the mineral collection at the University of California, Santa Barbara, and coptype material at the U.S. National Museum, Washington, D.C. and the Harvard Mineralogical Museum, Cambridge, Massachusetts.

Acknowledgments

References

Anderson, C. A. and Hinthorne, J. R. (1973) Thermodynamic approach to the quantitative interpretation of sputtered ion mass spectra. Analytical Chemistry, 45, 1421–1438.

Bell, C. K. (1963) X-ray examination of a Canadian occurrence of joaquinite. Geological Survey of Canada, Report MS 63-87.

Cannillo, E., Mazzi, F., and Rossi, G. (1972) The structure type of joaquinite. Tschermaks Mineralogische und Petrographische Mitteilungen, 17, 233–246.

Chihara, K., Komatsu, M., and Mizota, T. (1974) A joaquinite-like mineral from Ohmi, Niigata Prefecture, Central Japan. Mineralogical Journal, 7, 395–399.

Coleman, R. G. (1957) Mineralogy and petrology of the New Idria District, California. Ph.D. dissertation, Stanford University, California.

Dowty, E. (1975) Crystal structure of joaquinite. American Mineralogist, 60, 872–878.

Drake, M. J. and Weill, D. F. (1972) New rare earth element standards for electron microprobe analysis. Chemical Geology, 10, 179–181.

Hinthorne, J. R. and Anderson, C. A. (1975) Microanalysis of F and H in silicates with the ion microprobe mass analyzer. American Mineralogist, 60, 143–147.

Laird, J. and Albee, A. L. (1972) Chemical composition and physical, optical, and structural properties of benitoite, neptunite, and joaquinite. American Mineralogist, 57, 85–102.

Louderback, G. D. (1909) Benitoite, its paragenesis and mode of occurrence. University of California Publications, Bulletin of the Department of Geology, 5, 331–380.

Palache, C. and Foshag, W. F. (1932) The chemical nature of joaquinite. American Mineralogist, 17, 308–312.

Rucklidge, J. and Gasparrini, E. L. (1969) EMPADR 7, a computer program for processing electron microprobe analytical data. Department of Geology, University of Toronto.

Semenov, E. I., Bukin, Y. A., Balashov, and Sørensen, H. (1967) Rare earths in minerals of the joaquinite group. American Mineralogist, 52, 1762–1769.

Wise, W. S. and Gill, R. H. (1977) Minerals of the Benitoite Gem Mine. Mineralogical Record, 8, 442–452.