

CERITE FROM MOUNTAIN PASS, SAN BERNARDINO COUNTY, CALIFORNIA*

JEWELL J. GLASS, HOWARD T. EVANS, JR., M. K. CARRON, AND F. A. HILDEBRAND, *U. S. Geological Survey, Washington 25, D. C.*

ABSTRACT

Cerite, a silicate of cerium and lanthanum, occurs with bastnaesite in one of the rare-earth-bearing veins of the Mountain Pass district, California. The deposits of rare-earth minerals are in a mineralized zone in shonkinite in an area of Precambrian metamorphic rocks. The minerals associated with cerite are: bastnaesite, barite, quartz, chalcedony, calcite, galena, and altered acmite. Cerite is verona brown and occurs in massive form and in crystals. The crystals are pseudo-octahedral and range in size from 2 to 7 mm. The mineral has a resinous luster, a hardness greater than 5, and no observable cleavage. It gelatinizes in hot acid. The specific gravity as determined on the Berman microbalance is 4.78 ± 0.11 . The mineral is uniaxial positive, and the indices of refraction are $\omega = 1.806$ and $\epsilon = 1.808$. X-ray single-crystal studies show that the crystals are rhombohedral rather than orthorhombic as suggested by Nordenskiöld, and have the following characteristics: space group $R\bar{3}c(D_{3d}^6)$ or $R3c(C_{3v}^6)$; hexagonal $a = 10.78 \pm 0.08 \text{ \AA}$, $c = 38.03 \pm 0.27$. Crystal forms present are $c\{0003\}$, $e\{01\bar{1}2\}$. The chemical analysis of purified material, after about 4 per cent of impurities are subtracted, is interpreted in terms of chemical, physical and crystallographic properties to give the tentative formula: $(Ca, Mg)_z(RE)_8[(SiO_4)_{7-z}(FCO_3)_z][(OH)_z(H_2O)_{3-z}]$.

INTRODUCTION

The rare mineral cerite, a silicate of cerium and lanthanum, occurs in one of the rare-earth-bearing veins of the Mountain Pass district, San Bernardino County, California. This occurrence is the second known of this mineral in the United States. The first occurrence is near Jamestown in Boulder County, Colorado, and was described by Goddard and Glass (1940). Cerite was first discovered a century and a half ago at Bastnäs, Sweden (Hisinger and Berzelius, 1804, 1806) and the study of this new mineral led to the discovery of the element cerium. Since the discovery of cerite in Sweden at two places, two other minor occurrences have been recorded outside the United States: one in the Kyshtymsk (Kychtym) district in the Ural Mountains, Russia (Silberminz, 1929), and one in Papineau County, Quebec, Canada (Goddard and Glass, 1940). Cerite from Mountain Pass, California, was identified in the course of mineralogic and petrographic examinations of ore samples as a part of the investigation of rare-earth mineral deposits by the U. S. Geological Survey.

The Mountain Pass district, San Bernardino County, California, is traversed by U. S. Highway 91, about 35 miles east of Baker, and 60 miles southwest of Las Vegas, Nevada. The vein containing cerite is known as "Vein No. 6" in the Birthday group of claims, where the orig-

* Publication authorized by the Director, U. S. Geological Survey.

inal discovery of bastnaesite in the district was made in 1949. The specimens were taken from a prospect cutting the vein 200 ft. due east of the Birthday Vertical Shaft (Olsen, Shawe, Pray and Sharp, 1954, plate 10). Thus far, cerite has been found only in this vein, although it is not improbable that the mineral may be identified elsewhere in the district.

The specimens were provided by D. F. Hewett, U. S. Geological Survey. R. W. Lewis, Boulder City Station of the U. S. Bureau of Mines, courteously provided α -ray data made independently on duplicate specimens. W. T. Pecora, U. S. Geological Survey, contributed data on the geology. Several colleagues generously assisted in establishing the identification of cerite. Spectrographic examinations were made by K. J. Murata, H. J. Rose and E. L. Hufschmidt. J. M. Axelrod assisted in the α -ray diffraction studies. Appreciation is expressed also to the U. S. National Museum through whose cooperation specimens from other localities were secured for comparison. Finally, we wish to thank Dr. P. Gay of the University of Cambridge, who kindly gave us helpful information in connection with the crystallographic study.

GEOLOGY AND OCCURRENCE

The geology of the Mountain Pass district has been described by Sharp and Pray (1952) and by Olson, Shawe, Pray and Sharp (1954). The Mountain Pass district is in the northeastern part of San Bernardino County, about 12 miles from the Nevada state line. The Birthday claims are in the northern part of the district. Vein No. 6 is in the second quadrant from the upper right, S 1375, W 970, at 200 feet due east from the Birthday vertical, two-compartment shaft, map by Sharp and Pray (1952), and plate 10, Olson, Shawe, Pray and Sharp (1954). The region in which Vein No. 6 is found is characterized by Precambrian metamorphic rocks, including granite gneiss and mica schist. The dominant rock in the immediate area of Vein No. 6 is shonkinite, an alkalic rock that has intruded the metamorphic complex. Extensive alteration and replacement took place along fractures to form the quartz-barite-carbonate veins within which rare-earth minerals including cerite and bastnaesite are found.

The mineral assemblage in Vein No. 6 includes cerite, bastnaesite, barite, quartz, chalcedony, calcite, galena, and acmite. Hand specimens and thin sections show bastnaesite and quartz to be younger than cerite. Crystals of bastnaesite are locally perched on cerite in some cavities. In some areas the two minerals are intimately intergrown in indistinguishable relationships; in other areas the cerite and bastnaesite occur in parallel growth (Fig. 1).

A more detailed description of the associated minerals is given below:

Barite—Barite is one of the most abundant minerals in the cerite-bastnaesite-bearing vein. As much as 25 per cent of the vein materials is massive barite. Most of the barite is white, but some of it is stained pink; a little of it is colorless and transparent. Much of the barite has been dissolved, leaving a cavernous skeleton.

Bastnaesite—Bastnaesite, a fluocarbonate of cerium metals, occurs in Colorado at Jamestown in intimate association with the cerite, and at Pikes Peak, Allen and Comstock (1880), and at Bastnäs, Sweden. Geijer (1920, 1921) states for the cerite from Sweden, "There is, in fact, hardly

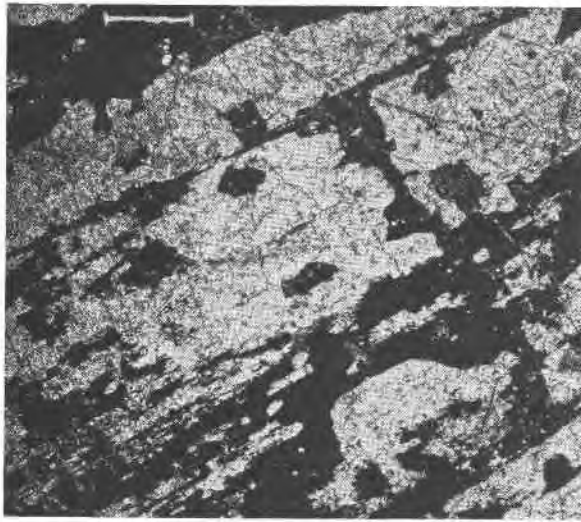


FIG. 1. Photomicrograph of a thin section of a specimen from vein No. 6, Mountain Pass, San Bernardino County, California, showing subparallel intergrowth of cerite (black) and bastnaesite (light gray). Crossed nicols; bar at top indicates 1 mm.

one thin section with any notable percentage of cerite that does not also contain bastnaesite, often making up one-third or more of the cerite ore." In the coarser cerite-bastnaesite vein material from Mountain Pass, the bastnaesite occurs in alternate bands with the cerite (Fig. 1) and in cavities in the barite and quartz. Small tabular crystals of pale-yellow, nearly colorless bastnaesite are found attached to the cerite crystals and commonly also attached to galena crystals. The variation in the types of occurrence and in the bastnaesite itself may be the result of repeated periods of hydrothermal action.

The interstitial bastnaesite has the following optical properties: the optic sign is uniaxial positive, and the indices of refraction are $\omega = 1.721$,

$\epsilon = 1.822$; the pale-yellow, nearly colorless crystals from cavities have the indices, $\omega = 1.718$, and $\epsilon = 1.818$.

Calcite—Glassy clear calcite is found in cavities in the barite and in the quartz. In places it occurs as part of the vein-filling mass.

Chalcedony—Opaline chalcedony was deposited late. It is found on the walls of cavities in the massive quartz, and as a covering over crystals of cerite and bastnaesite.

Galena—Galena crystals and aggregates of small crystals 5 mm. to 1 cm. across are found commonly in cavities loosely attached to the walls and partly replaced by quartz and bastnaesite. Nearly all the galena is covered completely by a crust of drusy bastnaesite, and the crust is shielded by a thin covering of chalcedony. The galena seems to be a relict that survived hydrothermal alteration.

Pyroxene—Extremely altered, high-index pyroxene that shows some of the properties of acmite is found in small patches of grayish-green fibers about 1 cm. long embedded in the quartz-barite areas of the vein material. It, like galena, seems to be a remnant of a preexisting rock.

Quartz—Quartz is the most abundant mineral in Vein No. 6. It is dull pinkish gray and finely crystalline. It shows the marks of severe attacks of invading solutions. In some areas the quartz is cavernous and serves as host rock for the other minerals.

The identification of cerite as a vein mineral in the Mountain Pass district adds to the list of rare-earth minerals identified in this district since the discovery of bastnaesite in 1949. Cerite is probably older than most of the bastnaesite in the same vein. Hydrothermal attack and formation of porous quartz and opaline chalcedony characterize the late mineralization in the vein. Cerite is a rare mineral in the district, and, if originally more widespread in distribution, it probably has disappeared by hydrothermal alteration.

PHYSICAL AND OPTICAL PROPERTIES OF CERITE

Cerite from Mountain Pass is verona brown (burnt umber) in color. Thin fragments are pale lavender brown to colorless. The mineral occurs massive and in crystals. The crystals have a pronounced pseudo-octahedral habit and vary in size from 2 mm. to 7 mm. across. They occur as clusters in cavities in the massive cerite, or as single crystals in a matrix of barite or calcite (Fig. 2 and Fig. 3). The mineral has an uneven fracture and no observable cleavage, a resinous luster, and a hardness slightly greater than 5. It gelatinizes in hot hydrochloric acid. Repeated

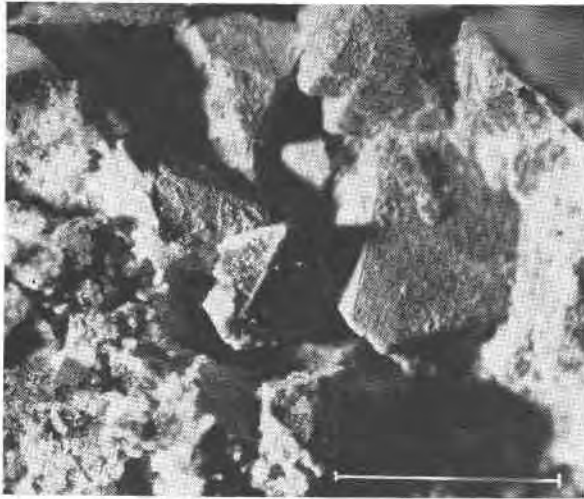


FIG. 2. Crystals of cerite in a cavity of drusy quartz from Mountain Pass, San Bernardino County, California. Direct light; bar indicates 1 cm.

determinations of the specific gravity of 10- to 20 mg. samples with the Berman balance yield an average value of 4.75 ± 0.11 . The variation among individual measurements is considerable, and suggests a poor crystalline texture.

Under the microscope, thin sections or thin fragments of the mineral are commonly sensibly isotropic. Thick grains vary from nearly isotropic

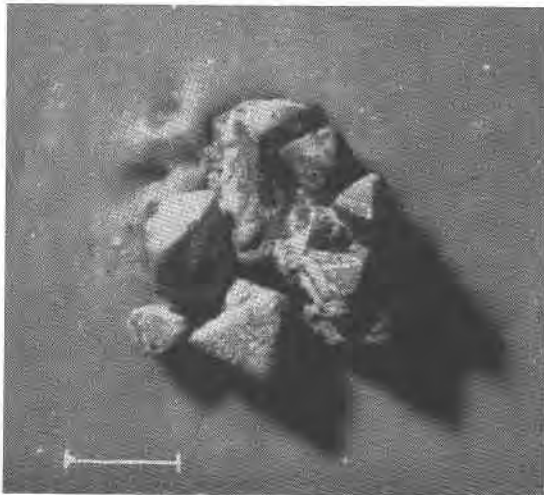


FIG. 3. Cluster of cerite crystals perched on massive cerite from Mountain Pass, San Bernardino County, California. Specimen mounted on wax. Bar indicates 1 cm.

to faintly anisotropic with undulatory extinction in the same grain, presumably resulting from internal strains. Under high magnification some grains revealed cloudy areas of included material, possibly bastnaesite, as this mineral is always detected in the x -ray powder patterns of cerite. Optical axial figures are seldom observed; they vary from uniaxial to very small 2V, biaxial positive. The indices of refraction are $\omega=1.806$, and $\epsilon=1.808$. Such low indices of refraction for cerite have not heretofore been noted. The optical properties of cerite from different places are compared in Table 1.

TABLE 1. COMPARISON OF OPTICAL PROPERTIES OF CERITE

	California 1	Colorado 2	Sweden 3	Sweden 4	Urals 5
α (ω)	1.806	1.815	—	1.817	1.810
β	—	1.815	1.81	1.818	—
γ (ϵ)	1.808	1.820	—	1.821	1.825
Birefringence	0.00-0.002	0.005	0.002	0.004	0.015
Sign	+	+	+	+	+
2V	0° to very small	0° to 8°	0° to small	25°	11°

1. This investigation.
2. Goddard and Glass (1940).
3. Geijer (1920, 1921).
4. Larsen and Berman (1934).
5. Silberminz (1929).

CRYSTALLOGRAPHY OF CERITE

Crystal fragments of cerite from Mountain Pass, California, were studied by the Buerger precession method. The crystals are rhombohedral, with the following crystallographic elements:

Space group: $R\bar{3}c$ (D_{3d}^6) or $R3c$ (C_{3v}^6)

Cell dimensions:

$$\left. \begin{aligned} a &= 10.78 \pm 0.08 \text{ \AA} \\ c &= 38.03 \pm 0.27 \\ a_R &= 14.12 \pm 0.11 \text{ \AA} \\ \alpha &= 45^\circ 07' \pm 57' \end{aligned} \right\} \begin{array}{l} \text{hexagonal} \\ \text{rhombohedral} \end{array}$$

Cell volume: $1280 \pm 16 \text{ \AA}^3$ (rhombohedral)

Morphological elements: $a:c=1:3.527$

$$p_0=4.072$$

Forms: $c\{0003\}$, $e\{01\bar{1}2\}$

The crystals are crudely formed, but the forms listed above can be identified. The forms are about equally developed, giving the crystals a pronounced pseudo-octahedral aspect, as shown in Fig. 4 ($c \wedge e = 66^\circ 17'$;

$e \wedge e = 80^\circ 0'$). The crystals appear holohedral in habit and give no positive piezoelectric response in the Giebe-Sheibe apparatus; therefore, the structure is probably centrosymmetric.

On the single crystal photographs, those reflections with l odd are absent for the $(h0l)$ reflections, owing to the glide plane; but in addition, for the (hkl) reflections, they are relatively weak and occur at large Bragg angles. Thus, the structure has a rhombohedral pseudocell, with $c = 19.08 \text{ \AA}$, one-half the true c axis length. The rhombohedral pseudolattice is in the negative mode with respect to the true lattice so that in this setting, the crystal form $e\{01\bar{1}2\}$ becomes the unit positive rhombohedron $\{10\bar{1}1\}$.

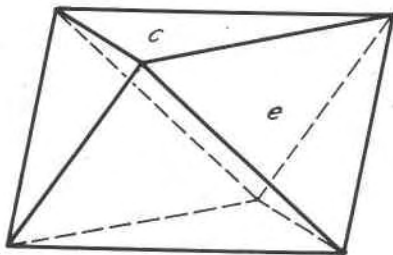


FIG. 4. Crystal habit of cerite from Mountain Pass, San Bernardino County, California. Crystal forms: $c\{0003\}$, $e\{01\bar{1}2\}$.

The powder diffraction pattern of Table 2 has been indexed on the basis of the true cell, but calculated spacings for reflections with l even only are listed. The powder pattern shows no clear evidence of metamict properties, and the pattern is virtually unchanged for a sample heated to 900° C .

In a recent short article by us (Glass, Evans, Carron and Rose, 1956), the Mountain Pass cerite was described as monoclinic. Following a kind personal communication from P. Gay of Cambridge, England, who has made a new study of cerite from Bastnäs (Gay, 1957*b*), the higher rhombohedral symmetry for the California material was found in the single crystal photographs (Gay, 1957*a*). The primitive unit cell of the rhombohedral lattice defined here and the body-centered monoclinic lattice assumed earlier have equivalent dimensions and the same volume. Gay (1957*a*) has pointed out that there is a possibility that the hexagonal lattice is primitive rather than rhombohedrally centered, but no trace of any reflections that would support such a hypothesis has been found on the many precession photographs made of the Mountain Pass crystals.

The single crystal diffraction patterns were made from euhedral fragments about 1 mm. in cross section. Because of the moderate distortion of the texture of the crystal, smaller fragments did not give any im-

TABLE 2. POWDER-DIFFRACTION DATA FOR CERITE

Calculated spacings based on rhombohedral cell, space group $R\bar{3}c$ (or $R3c$); hexagonal $a=10.78$, $c=36.03$ Å, $l=2n$ only.

Measured spacings based on F. A. Hildebrand film no. 8689, $\text{FeK}\alpha$ radiation, 114.7 mm. diameter camera, cutoff 17.0 Å.

<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i>
01.2	8.39	8.40	13	40.10	1.990		
10.4	6.66	6.67	7	21.16	1.972		
00.6	6.34	6.35	6	11.18	1.967		
11.0	5.39	5.40	9	23.8	1.954	1.954	50
20.2	4.53	4.53	17	41.6	1.947	1.939	13
01.8	4.24	4.23	12	31.14	1.870		
02.4	4.19			32.10	1.867		
11.6	4.10			50.2	1.865		
10.10	3.523	3.51	15	01.20	1.864	1.863	25
12.2	3.472	3.47	42	05.4	1.839	1.834	12
20.8	3.332			33.0	1.798	1.799	15
21.4	3.310	3.31	33			1.791	5
00.12	3.170	3.17	7	20.20	1.766		
30.0	3.113	3.11	30	13.16	1.752		
02.10	2.949	2.95	100	30.18	1.748	1.748	25
12.8	2.835	2.83	38	24.4	1.741		
30.6	2.795	2.80	27	50.8	1.739	1.740	9
11.12	2.733			33.6	1.729		
22.0	2.696	2.69	42	14.12	1.720	1.717	5
01.14	2.596			10.22	1.700		
21.10	2.587	2.59	21	05.10	1.683		
31.2	2.567	2.57	7	23.14	1.679	1.679	10
13.4	2.500	2.50	5	15.2	1.677		
22.6	2.482	2.44	3	12.20	1.674		
20.14	2.349			40.16	1.666		
04.2	2.318	2.31	7	22.18	1.663		
10.16	2.304			42.8	1.655	1.655	7
31.8	2.275	2.27	7	02.22	1.622		
40.4	2.267			32.16	1.592	1.593	13
30.12	2.222	2.22	25	15.8	1.587		
12.14	2.146			00.24	1.585	1.583	8
13.10	2.141	2.14	9	21.22	1.553	1.566	9
23.2	2.130			50.14	1.537	1.535	8
02.16	2.119	2.13	7			1.515	6
00.18	2.113					1.496	8
04.8	2.096	2.09	12			1.456	7
32.4	2.090	2.07	5			1.424	12
41.0	2.045	2.04	9				

provement in the somewhat crude appearance of the patterns. The precession patterns showed several powder rings in addition to the spot patterns of cerite. The ring pattern, which is characterized in Table 3,

TABLE 3. POWDER-DIFFRACTION RINGS ON CERITE PRECESSION PATTERNS
Indexed for bastnaesite with $a=7.14$, $c=9.78$ Å

Line no.	<i>I</i>	<i>d</i> (obs)	<i>d</i> (calc.)	<i>hkl</i>
1	SO	4.94 Å	4.89 Å	00.2
2	W	3.57	3.57	11.0
3	WM	2.88	2.88	11.2
4	MO	2.44	2.44	00.4
5	W	2.05	2.06	30.0

S=strong, M=medium, W=weak, O=oriented.

has been identified with bastnaesite. In order to confirm the identification, a powder diffraction pattern of bastnaesite from Mountain Pass has been measured and indexed as shown in Table 4. (Because of the special positions which the heavy scatterers—the cerium atoms—have in the bastnaesite structure, powder lines for the class of reflections for which $(h-k)=3n$ and $l=2n$ only are to be expected, except for a few weak lines at low Bragg angles.) Two of the bastnaesite powder rings which appear on the cerite single crystal patterns, namely (00.2) and (00.4), are strongly concentrated in certain directions. This preferred orientation effect is such as to indicate that the bastnaesite is the light-colored coating visible on the surface of the cerite crystals, and is strongly oriented with the hexagonal c axis tending to lie normal to the crystal surfaces.

Nordenskiöld (1873) has described the morphology of crystals of cerite from Bastnäs, Sweden, and the System of Mineralogy (Dana, 1896) follows this description. The habit and crystallography (orthorhombic) of Nordenskiöld's crystals bear no resemblance whatever to that found for Mountain Pass crystals. On the other hand, the x -ray powder patterns obtained for cerite from Mountain Pass, Jamestown, and Bastnäs are all identical (if the varying admixture of bastnaesite is taken into consideration). Professor Clifford Frondel of Harvard University very kindly loaned us a specimen of the type material from Bastnäs, which was presented to the Harvard museum by Berzelius in 1807. A powder pattern of cerite from this specimen again proved to be identical to that of the Mountain Pass cerite, with a fairly strong bastnaesite pattern superposed. In light of the accumulated evidence, the identity of cerite cannot be doubted. Nordenskiöld's crystallographic measurements cannot be reconciled with ours.

CHEMISTRY OF CERITE

Observations made on specimens from all the known deposits of cerite show that the mineral habitually occurs with some other cerium earth

TABLE 4.—POWDER-DIFFRACTION DATA FOR BASTNAESITE, BIRTHDAY CLAIM, MOUNTAIN PASS, CALIF.
Hildebrand film No. 5888, Hexagonal, $P6_2c$, $a=7.129$ $c=9.774$ Å; $CuK\alpha$ radiation, d cutoff at 12.0 Å.

$hk \cdot l$	d (calc.)	d (obs.)	I	$hk \cdot l$	d (calc.)	d (obs.)	I
00.2	4.887	4.881	42	22.8	1.0087}	1.006	6
11.0	3.564	3.564	71	60.2	1.0073}		
11.2	2.880	2.879	100	52.0	.9886	.988	3
20.2*	2.609	2.610	1	00.10	.9774		
00.4	2.445	2.445	9	52.2	.9689	.9689	7
10.4*	2.272	2.273	3	33.6	.9599	.9585	2
20.3*	2.241	2.238	3	60.4	.9482	.9480	3
30.0	2.058	2.057	42	11.10	.9427	.9425	3
11.4	2.016	2.016	42	52.4	.9164	.9162	5
30.2	1.898	1.898	42	41.8	.9050	.9048	5
22.0	1.782	1.783	9	44.0	.8911	.8908	2
22.2	1.674	1.674	21	30.10	.8829	.8827	2
00.6	1.629	1.629	1	44.2	.8766	.8766	3
30.4	1.574	1.573	15	60.6	.8699	.8701	3
11.6	1.482	1.481	9	22.10	.8569	.8569	3
22.4	1.440	1.439	11	33.8	.8518	.8520	3
41.0	1.347	1.347	7	52.6	.8451	.8451	5
41.2	1.299	1.298	15	44.4	.8372	.8369	3
30.6	1.277	1.277	7	71.0	.8176	.8175	3
00.8	1.222	1.223	2	00.12	.8145	.8070	6
22.6	1.203	1.204	6	11.12	.7921	.7920	4
33.0	1.189	1.190	3	41.10	.7892	.7892	6
41.4	1.180	1.180	9	60.8	.7851	.7851	3
11.8	1.156}	1.156	11	44.6	.7799	.7799	4
33.2	1.155}			63.0	.7760	.7760	5
33.4	1.069	1.068	4	71.4	.7737	.7737	7
30.8	1.051	1.050	4				
41.6	1.038	1.038	6				
60.0	1.029	1.028	2				

Note: All Reflections for which $l=2n$ and $(h-k)=3m$ are calculated, plus those marked (*). d (obs.) corrected for film shrinkage of 0.216%.

mineral. At Mountain Pass, bastnaesite is the principal contaminant, from which it is very difficult to separate the cerite.

To prepare cerite for chemical analysis, a sample that weighed 103 grams was selected from a part of Vein No. 6 that showed the greatest concentration of cerite. The sample was crushed to pass 40 mesh and after the fine fraction (-200) was screened off, the light minerals were removed by floatation with methylene iodide (specific gravity 3.3). The heavy concentrate consisted of cerite and bastnaesite. The free grains of yellow bastnaesite were removed by hand-picking. The remaining grains that contained both cerite and bastnaesite were crushed and separated

into two fractions, one $-80+100$ mesh, and another, $-100+200$ mesh. These fractions were separated by passing them through the Frantz isodynamic magnetic separator. The optimum tilt and pitch of the separator, which were slightly different for each of the two size fractions, were determined by trial. After the two fractions were passed through

TABLE 5. CHEMICAL ANALYSIS OF CERITE FROM MOUNTAIN PASS,
SAN BERNARDINO COUNTY, CALIFORNIA

Constituent	1	2	3	4
Ce ₂ O ₃	35.73		37.3	.397
La ₂ O ₃ etc.	31.53		32.9	.350
SiO ₂	18.46	2.00	17.2	1.000
CaO	3.72		3.9	.24
MgO	1.58		1.6	.14
H ₂ O ⁻	0.14	0.14		
H ₂ O ⁺	2.26		2.4	.46
CO ₂	3.56		3.7	.30
F	1.60		1.7	.31
Al ₂ O ₃	0.95	0.95		
Fe ₂ O ₃	0.76	0.76		
TiO ₂	0.07	0.07		
Na ₂ O	0.20	0.20		
K ₂ O	0.13	0.13		
MnO	0.17	0.17		
BaO	0.37	0.37		
SO ₃	0.12	0.12		
Total	101.35		100.7	
Less O=2F	-0.67		-0.7	
Corr. total	100.68		100.0	

1. Gross analysis on purified sample; M. K. Carron, analyst.
2. Subtractions for impurities: 1 per cent SiO₂ as chalcedony; 3.28 per cent SiO₂, Al₂O₃, Fe₂O₃, TiO₂, Na₂O, K₂O and MnO as altered acmite and unidentifiable alteration products; 0.49 per cent BaO and SO₃ as barite; 0.14 per cent H₂O(-) as moisture.
3. Corrected analysis with fluocarbonate included, recalculated to 100%.
4. Mol ratios calculated from column 3, with SiO₂ set equal to 1.000. Molecular weight of La₂O₃, etc. is taken as 328.5.

the separator nineteen times and recombined with the fine fraction, the remaining 4 grams of cerite were considered sufficiently pure for chemical analysis.

The complete chemical analysis of cerite from Mountain Pass prepared as described above is given in Table 5, column 1. The analysis corrected for about 5 per cent of impurities (Table 5, column 3), is compared with

previously reported analyses in Table 6. A quantitative spectrographic analysis of the rare earths was made by H. J. Rose, Jr.; the results are shown in Table 7.

The problem of assigning a formula to cerite has always been complicated both by the great difficulty of purification and by the inherent

TABLE 6. CHEMICAL ANALYSES OF CERITE

Constituent	1	2	3	4	5	6
Ce ₂ O ₃	37.3	32.97	24.06	33.25	33.65	31.37
La ₂ O ₃ , etc.	32.9	35.72	35.37	34.60	37.49	38.64
SiO ₂	17.2	18.10	22.79	18.18	15.60	21.24
CaO	3.9	5.80	4.35	1.69	1.27	2.97
MgO	1.6	0.21			0.07	1.88
H ₂ O	2.4(+)	1.26	3.44	5.18	1.48	2.10
CO ₂	3.7				7.86	.30
F	1.7				0.94	1.47
Y ₂ O ₃		3.86				
Al ₂ O ₃		0.32	1.26		0.50	
Fe ₂ O ₃					0.28	0.43
FeO		1.54	3.92	3.18		0.68
MnO		0.22			0.15	
(Na, K) ₂ O					0.15	
Gangue			4.33			
Total	100.7				99.44	101.08
Less O=2F	-0.7				-0.40	-0.62
Corr. total	100.0	100.0	99.52	96.08	99.04	100.46

1. Cerite from California, from column 3, Table 5 (M. K. Carron, analyst); 4.9% impurities subtracted and recalculated to 100%.
2. Cerite from Colorado, J. G. Fairchild, analyst (Goddard and Glass, 1940); 23.8% impurities subtracted and recalculated to 100%.
3. Cerite from Bastnäs, G. Nordström, analyst (Nordenskiöld, 1873).
4. Cerite from Bastnäs, L. Kettner, analyst (Stolba, 1879).
5. Cerite from Kychtym (Urals) (Silberminz, 1929).
6. Cerite from Bastnäs, J. H. Scoon, analyst (Gay, 1957b).

NOTE: An analysis of cerite from Jamestown, Colorado, has also been published by Hanson and Pearce (1941), but is not considered here because of the questionably high percentage of alumina (14.6%) reported.

variability of composition of the mineral itself. Most troublesome in this regard is the intimate admixture of bastnaesite with cerite which is almost universal. It has not been possible to obtain an x-ray powder diffraction pattern of cerite that is completely free of bastnaesite lines, although the material from Mountain Pass purified for analysis shows

bastnaesite lines in its powder pattern only in traces. We are faced with the question, therefore, of whether the fluocarbonate which usually appears in the analyses is to be wholly associated with bastnaesite, or partly with bastnaesite and partly with cerite. The presence of minor amounts of other impurities can also be seen optically in the Mountain Pass material as a finely disseminated phase, perhaps a fine-grained alteration product, penetrating the cracks and fissures in the cerite

TABLE 7. SPECTROGRAPHIC ANALYSIS OF THE TOTAL RARE EARTHS EXTRACTED FROM CERITE OF MOUNTAIN PASS, SAN BERNARDINO COUNTY, CALIFORNIA
(H. J. Rose, Jr., Analyst)

	Wt. per cent of total rare earths
La ₂ O ₃	22.40
CeO ₂	54.30 (chemical)
Pr ₆ O ₁₁	5.80
Nd ₂ O ₃	17.30
Sm ₂ O ₃	1.60
Y ₂ O ₃	.69
Gd ₂ O ₃	0*
	<hr/> 102.09

* Gd₂O₃ not detected; less than 1 per cent.

grains. The nature of these impurities is unknown, but their influence on the analytical data is probably minor.

In attempting to interpret the chemical analysis of cerite in terms of the crystallography, it was assumed, first, that all of the fluocarbonate is included in the cerite formula; and, second, that none of it is included, but is to be subtracted from the analysis as bastnaesite. In the second case, no formula consistent with the crystallography and other evidence could be found, but, as will be shown, a satisfactory formula was evolved with the first assumption. For this reason, and also because, in the carefully prepared samples that were analyzed no significant amounts of bastnaesite could be detected by physical means, the following discussion is based on the assumption that fluocarbonate is an essential constituent of the cerite formula.

The crystallography places few restrictions on the composition of cerite because of the large size of the unit cell, but the following points must be considered. The molecular weight of the hexagonal cell contents as derived from the measured specific gravity is $11,000 \pm 400$. The

rhombohedral symmetry demands that the largest formula weight be one-third of this, or 3780 ± 140 . The only other restriction on the formula arises from the nature of the pseudo-cell, which is also rhombohedral but has a *c* axis one half of that of the true cell. We may conclude from the fact that the true cell is revealed by weak single crystal reflections which appear only above a moderately large Bragg angle, that the heavy atoms, at least, must occupy the pseudo-cell in multiples of 3. Therefore, we will

TABLE 8. CHEMICAL COMPOSITION OF CERITE CALCULATED FROM UNIT CELL CONTENT

Component	Mountain Pass			Bastnäs		
	Formulas per cell	Wt. % calc.	Wt. % obs. ³	Formulas per cell	Wt. % calc.	Wt. % obs. ⁴
(RE) ₂ O ₃ ¹	24	70.3	70.1	24	69.7	70.0
CaO	7.5	3.7	3.9	6.4	3.2	3.2
MgO	4.5	1.6	1.6	5.6	2.0	2.0
SiO ₂	32.5	17.6	17.2	42	22.3	22.6
CO ₂	9.5	3.7	3.7	18	2.8	2.2
F		1.6	1.7			
H ₂ O	13.2 ²	2.1	2.5			
Mol. wt.	11,219			11,319		
Specific volume oxygen	19.9			19.9		
Specific gravity	4.78 (meas.)			4.89 (meas.)		
	4.86 (calc., x-ray)			4.92 (calc., x-ray)		
	4.87 (calc., optics)			4.91 (calc., optics)		
Formula:	(Ca, Mg) ₂ (RE) ₈ (SiO ₄ , FCO ₃) ₇ (OH, H ₂ O) ₃					

¹ RE represents Y, La, Ce, etc.

² 13.2 H₂O equivalent to 8.5 H₂O + 9.5 (OH)⁻ = 18[(OH), H₂O]

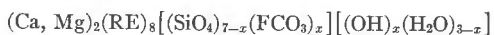
³ From Table 6, column 1.

⁴ From Table 6, column 6: 1.57 per cent bastnaesite and 4.70 per cent fluocerite subtracted and recalculated to 100 per cent.

expect the number of cations in the true cell to be present in multiples of 6.

In Table 8, the analysis of the Mountain Pass cerite and also the new analysis of the Bastnäs material reported by Gay (1957*b*) are interpreted in terms of the contents of the true hexagonal unit cell. It is found that the various conditions are met if Ca⁺² and Mg⁺² are in solid solution on the one hand, and (FCO₃)⁻³ and (SiO₄)⁻⁴ on the other, the latter with concomitant substitution of (OH)⁻ for H₂O. In the Bastnäs analysis given in Table 6, column 6, 1.47 per cent F was reported with only 0.30

per cent CO₂, but because the silicate positions appear to be fully occupied by (SiO₄)⁻⁴ groups, there is no way to fit this fluoride into the formula. Therefore, the excess F has been subtracted as fluorcerite (somewhat arbitrarily) in Table 8. With these assumptions and adjustments it is found that a surprisingly good match is obtained in both cases for measured specific gravities, and those calculated both from unit cell contents and from refractive indices by the law of Gladstone and Dale (Jaffe, 1957). The formula proposed for cerite is:



For the Mountain Pass sample, $x=1.6$ and for the Bastnäs material, $x=0$.

The substitutions postulated in the formula are uncommon, but not unprecedented. Because of the disparity in ionic radii, magnesium usually replaces calcium only in minor amounts, but in cerite the replacement apparently amounts to almost 50 mol per cent. Such replacement may be expected in structures where the calcium site involved is not a primary feature of the structure, and where adjustments are possible that will cause the coordination to become more nearly octahedral as the substitution of magnesium is increased. The best example of this type of substitution is garnet (Ca, Mg₃Al₂(SiO₄)₃), in which extensive replacement is often evident. Gay (1957*b*) considers the calcium and magnesium to be in partial replacement of the rare-earth component, but the present indications of the analytical interpretation are that they play a separate role.

The hypothesis of the substitution of carbonate, or a fluocarbonate complex, for orthosilicate is more problematical, but not wholly unreasonable. A similar situation has been observed in apatite, which sometimes has been found to contain a considerable amount of carbonate. The role of carbonate in apatite (francolite) has been somewhat controversial (Palache, Berman, and Frondel, 1951, p. 882), but the only reasonable substitution mechanism would be the replacement of the tetrahedral PO₄⁻⁴ group by CO₃⁻² or a tetrahedral combination such as CO₃⁻²+F⁻ or CO₃⁻²+OH⁻. The unusual apatites from Crestmore, California (wilkeite and ellestadite, Palache, Berman, and Frondel, 1951, pp. 905-6) indicate that PO₄⁻³, SO₄⁻², SiO₄⁻⁴ and CO₃⁻² may all replace each other extensively in the apatite structure. Although we accept the substitution of carbonate for silicate in cerite, the possibility that fluoride plays a role collateral with carbonate is less clear cut. In the Bastnäs analysis, where carbonate is insignificant, as stated earlier, there seems to be no way to fit the fluoride into the formula.

The formula proposed for cerite by Gay (1957*b*), (Ca, Mg, RE)₃Si₂(O, OH, F)₉, must be taken 20 or 21 times to fill the unit cell, and therefore

must constitute only an approximation to the true formula. The formula presented by us, although satisfying all of the conditions imposed by the chemical, physical and crystallographic measurements, must also be regarded as tentative, in view of the assumptions and corrections made in interpreting the data. The true formula of cerite will probably be revealed only by a complete crystal-structure determination.

REFERENCES

- ALLEN, O. D., AND COMSTOCK, W. J. (1880), Bastnaesite and tysonite from Colorado: *Am. Jour. Sci.*, **19**, 390-393.
- DANA, E. S. (1896), System of mineralogy, 6th ed.: John Wiley and Sons, Inc., New York, N. Y.; p. 550.
- GAY, P. (1957a), The crystallography of cerite: *Am. Mineral.*, **42**, 429-432.
- (1957b), An x-ray investigation of some rare-earth silicates: cerite, lessingite, becke-lite, britholite, and stillwellite: *Min. Mag.*, **31**, 455-469.
- GEIJER, PER (1920, 1921), The cerium minerals of Bastnäs at Riddarhyttan: *Sveriges geol. undersökning, Arsbok*, **14**, 15.
- GLASS, J. J., EVANS, H. T., JR., CARRON, M. K., AND ROSE, H. (1956), Cerite from Mountain Pass, San Bernardino County, California: *Am. Mineral.*, **41**, 665.
- GODDARD, E. N., AND GLASS, J. J. (1940), Radioactive cerite from near Jamestown, Colorado: *Am. Mineral.*, **25**, 381-404.
- HANSON, R. A., AND PEARCE, D. W. (1941), Colorado cerite: *Am. Mineral.*, **26**, 110-120.
- HISINGER, W., AND BERZELIUS, J. (1804), Cerium, ein neues Metall aus einer schwedischen Steinart, Bastnäs Tungstein genannt: *Neues Allg. Jour. Chemie*, **2**, 397-418.
- , (1806), Undersökning af Cerium, en ny metall funnen i Bastnäs Tungsten: *Afhandlingar i Fysik, Kemi och Mineralogi*, **1**, 58-84.
- JAFFE, H. W. (1956), Application of the rule of Gladstone and Dale: *Am. Mineral.*, **41**, 757-777.
- LARSEN, E. S., JR., AND BERMAN, H. (1934), The microscopic determination of the non-opaque minerals: *U. S. Geol. Survey Bull.*, **848**, 140.
- ŖORDENSKIÖLD, A. M. (1873), Om ceritins kristallform: *Öfv. Ak. Stockh.*, **30**, 13-16.
- OLSON, J. C., SHAW, D. R., PRAY, L. C., AND SHARP, W. N. (1954), Rare-earth mineral deposits of the Mountain Pass district, San Bernardino County, California: *U. S. Geol. Survey Prof. Paper* **261**.
- PALACHE, E., BERMAN, H., AND FRONDEL, C. (1951), Dana's System of Mineralogy, 7th ed., vol. 2: John Wiley and Sons, Inc., New York, N. Y.
- SHARP, W. N., AND PRAY, L. C. (1952), Geologic map of the bastnaesite deposits of the Birthday claims, San Bernardino County, Calif.: *U. S. Geol. Survey, Min. Inv., Field Studies*, **MF-4**.
- SILBERMINZ, V. (1929), Sur le gisement de cerite de bastnaesite et d'un mineral nouveau, la lessingite dans le district de Kychtym (Oural): *Acad. Sci., U.S.S.R., C.R. A*, **55**; *Abs.* (1930), *Neues Jahrb. Min.*, **1**, 123.
- STOLBA, F. (1879), Zur Kenntnis der Zusammensetzung des Cerits von Bastnäs: *K. böhm. Gesell. Wiss.*, **1879**, 372.