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A CERIAN VESUVIANITE FROM CALIFORNIA

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ABSTRACT

A variety of vesuvianite containing a high percentage of cerium and other rare earth elements, and having unusually high specific gravity and refractive indices, has been found in altered greenstone of Franciscan (?) age, near the Dallas benitoite mine, San Benito County, California. The mineral occurs sparsely distributed as minute amber to deep red-brown prisms in veins in the greenstone, associated with abundant black garnet, chlorite, and occasional perovskite. The crystals seldom have terminal faces, but when these are present, have the usual vesuvianite habit of prisms and unit pyramids. {001} is rare, even on terminated crystals.

The ratio c:a = 0.7437. Single crystal study confirms the vesuvianite unit cell, with $a = 15.97$ Å, $c = 11.90$ Å. space group D_{4h}^{4}, P^{4}/nnc. Optically, $\omega = 1.7617$, $\epsilon = 1.7498$, measured in Na light, abnormally high for vesuvianite. G = 3.60.

Chemical analysis is as follows: CaO 27.5, MgO 3.0, RE_2O_3 (total) 16.7, Al_2O_3 9.3, total Fe as Fe_2O_3 5.4, TiO_2 5.5, SiO_2 33.1, CO_2 0.59, F < 0.1, $H_2O(-) < 0.1$, $H_2O(+)$ 1.0. This analysis fits the vesuvianite formula. Of the rare earths, Ce is major, Y, La and Nd considerable and eleven others in much less amounts.

OCCURRENCE

A mineral recently observed associated with one of the black garnet occurrences (NE $\frac{1}{4}$ sec. 35, T. 18 S, R. 12 E, MDM) near the Dallas benitoite mine in San Benito County, California, was submitted to one of us (J. M.), with the question of whether it might be some rare mineral. Preliminary examination showed it to be very high in cerium and other rare-earth elements, and careful study has indicated that it is an unusual vesuvianite, containing far greater amounts of the rare earths than any previously described.

The mineral occurs along the surfaces of fissures in altered greenstone of Franciscan(?) age, normally as isolated crystals, less commonly as clusters of crystals. It is associated with a number of minerals, some of which are unusual; commonest of these is melanite garnet in crystals and massive veins. There are also local nests of crystalline chlorite, and a white bladed mineral close to diopside in properties. Perovskite of two types has been noted in the veins: one of these is in flesh-colored octahedral crystals or somewhat shapeless grains, and the other is black, in shiny cubes or dull, corroded, locally almost spongy octahedra. Apatite is rarely present, in minute, white prisms.

In association with the garnet, vesuvianite usually is distinctly later, although in places it is present as prisms piercing, or partly embedded

in, the garnet crystals. Where with chlorite, it occurs as crystals perched on crystalline crusts of the chlorite. Its relations with perovskite are not clear, as the two minerals rarely are side by side.

Physical and Optical Properties

This vesuvianite is invariably in prismatic crystals, ranging from minute up to one by two millimeters, but usually smaller, the smaller crystals being rather more slender. The mineral is non-pleochroic, and ranges in color from clear amber to red-brown, locally so dark as to be nearly black. Euhedral terminations are rare, and usually only prism faces are present. Commonly the prisms are longitudinally striated, due to the presence of many line-faces. In many crystals, the termination is cupped, with the face-junctions forming spines around the rim of the cup.

Table 1. Cerian Vesuvianite Angle Table
Tetragonal bipyramidal—$P4/nnc$, D_{4h}^4
$a:c$—1:0.7539 $P_0:r_0$=0.7539:1

		ϕ	ρ	A	$\overline{M}$
c	001	—	0° 00′	90° 00′	90° 00′
a	010	0° 00′	90 00	90 00	45 00
m	110	45 00	90 00	45 00	90 00
k	150	11 49	90 00	78 11	56 49
h	130	18 26	90 00	71 34	63 26
f	120	26 34	90 00	63 26	71 34
e	101	90 00	37 00½	52 59½	115 48
u	121	26 34	59 20	67 22	74 12

Specific gravity determined on the Berman balance, is 3.60. Hardness is between 5 and 6. Cleavage was not observed. It is insoluble in acids and fusible easily to a black glassy bead.

Optically it is uniaxial negative, with $\omega = 1.7617$, and $\epsilon = 1.7498$, both ± 0.0005, values determined in sodium light.

Many of these properties are abnormal for vesuvianite and their values are presumably due to the unusual composition of this material. For example, the specific gravity is considerably above the higher values cited in the literature (3.43), and ϵ and ω are also far above the usual values, $\epsilon = 1.746$, $\omega = 1.752$ (Deer *et al.*, 1962, Vol. I, 116).

Crystallography

A number of terminated crystals have been measured on the two-circle goniometer, confirming its relationship to normal vesuvianite.

The crystals are tetragonal, with the prisms (110) and (100) usually

dominant. (130) and (120) appear as narrow faces, and are generally present, sometimes measurable, but generally in combination locally with (150) producing longitudinal striations on the slender prismatic crystals. Terminal faces, rather infrequent, are (101) and (121), usually both present, and (001), much less common. The ratio c/a from crystal measurements is 0.7536, closely matching the axial ratio derived from x-ray single crystal measurements. Both in habit and angular values, it is very close to normal vesuvianite. The calculated values of the angle table (Table 1), agree satisfactorily with the angles measured on the crystals.

Chemistry

About 140 mg of carefully hand-picked mineral was available for analysis. A spectrographic analysis[1] was used as a guide for the chemical analysis. Only those elements greater than 0.1% were determined chemically.

Methods of Analysis

Ca, Mg, Ti, Fe, and Rare Earths. A 25 mg sample was treated with HF, precipitating rare-earth fluorides together with some calcium. The rare-earth elements were separated from Ca by NH_4OH precipitations to phenolphthalein end-point and were determined gravimetrically as a group. The combined filtrates (HF and NH_4OH precipitations) were used to determine Ca, Mg, Ti and Fe. Mg was determined spectrophotometrically with thiazole yellow, Ti with tiron, and Fe with o-phenanthroline. Total Ca and Mg were determined by a versene titration and a Ca value calculated.

Cerium was determined on a separate 40 mg sample. Cerium was oxidized with $NaBiO_3$, reduced with excess standard Fe $SO_4(NH_4)_2SO_4$ solution and the excess titrated with standard $K_2Cr_2O_7$ solution.

Si and Al. Five milligram samples were decomposed by NaOH fusion in gold crucibles. Silicon was determined spectrophotometrically by a molybdenum blue procedure and Al with alizarin red S.

F. Determined spectrophotometrically with thoron using a 20 mg sample.

H_2O and CO_2. Forty milligram sample ignited at 900° C. and CO_2 and H_2O were absorbed and weighed.

[1] Analyst, C. L. Waring. U. S. Geological Survey, Washington, D. C.

The results of the analysis together with an analysis from the U.S.S.R. are shown in Table 2. The analysis by Orlov and Mart'yanov (1961) gives the highest rare earth value previously recorded for vesuvianite.

The analysis fits the general vesuvianite formula, $Ca_{10}(Mg, Fe)_2 Al_4 Si_9 O_{34} (OH)_4$, quite well considering the small amount of sample that was available for analysis. Table 3 shows the calculation of the formula

TABLE 2. CHEMICAL ANALYSIS OF VESUVIANITE

Constituents	Weight Percent	
	1	2
CaO	30.84	27.5
RE_2O_3	4.31[1]	16.7
(Ce_2O_3)		(4.1)
Al_2O_3	12.47	9.3
Fe_2O_3	3.06	5.4[2]
FeO	5.6	
MnO	0.32	
MgO	1.42	3.0
TiO_2	3.88	5.5
Na_2O	0.53	
K_2O	0.15	
SiO_2	34.59	33.1
CO_2		.59
F		<.10
H_2O-	.05	<.10
H_2O+	2.19	1.0
	99.41	102.3

1. Rare-earth vesuvianite from the Enisei Mountain Range, Orlov and Mart'yanov (1961).

2. Cerian vesuvianite from California, analyst Blanche L. Ingram, U. S. Geological Survey, Washington, D. C.

[1] Rare earths, determined by *x*-ray spectrographic analysis: Ce 48, La 24; Pr 5.4, Nd 16.0, Sm 1.8, Eu 0.02, Gd 1.2, Tb 0.2, Dy 0.4, Er 0.3 Yb 0.2, Y 3.0.

[2] Total Fe as Fe_2O_3.

from the chemical data. Insufficient rare-earth oxides were available for a quantitative spectrographic analysis of the individual rare-earth elements, but an analysis was attempted with the 4 mg of oxides available from the chemical analysis. Table 4, showing the spectrographic analysis of the oxides, is given only to indicate an approximate composition.

X-RAY STUDY

An *x*-ray powder pattern of vesuvianite, shown in Table 5, using copper radiation, $\lambda = 1.5418$ Å, has been indexed down to $d = 1.567$ Å.

TABLE 3. CALCULATION OF FORMULA

Vesuvianite = Ca_{10} $(Mg,Fe)_2$ Al_4 Si_9 O_{34} $(OH)_4$

Constituent	Weight Percent	Molecular Ratios	Ions×10	Ions
CaO	27.5	0.4904	Ca 4.904	7.80
RE_2O_3	16.7	0.0506[1]	R.E. 1.012	1.61
(Ce_2O_3	4.1)			9.41
Al_2O_3	9.3	0.0913	Al 1.826	2.91
Total Fe as Fe_2O_3	5.4	0.0338	Fe .670	1.08
MgO	3.0	0.0740	Mg .740	1.18
TiO_2	5.5	0.0686	Ti .686	1.09
				6.26
SiO_2	33.1	0.5517	Si 5.517	8.78
F	<0.1			
CO_2	0.59			
H_2O-	<0.1			
H_2O+	1.0	0.0555	OH 1.110=set sum	1.77
			O 22.766 38	36.23
				38.00

[1] Average molecular wt. of 319.19 used for rare earth oxides which is a weight representative of the major constituents: Ce, Nd, La and Y.

The close similarity to ordinary vesuvianite is shown by the accompanying pattern of a specimen from northeastern Brazil.

Single-crystal rotation and layer-line Weissenberg photographs, about c, give the following space group and cell dimensions: $a = 15.97$, $c = 11.90$

TABLE 4. SPECTROGRAPHIC ANALYSIS OF THE RARE-EARTHS

Oxides>10%	Oxides 1–10%	Oxides<1%
Ce	Y	Eu
	La	Tb
	Pr	Dy
	Nd	Ho
	Sm	Er
	Gd	Tm
		Yb
		Lu

Analyst, Sol Berman, U. S. Geological Survey, Washington, D. C. Analysis based on a 4 mg sample of the oxides from the chemical analysis.

TABLE 5. VESUVIANITE, *X*-RAY POWER DATA, COPPER RADIATION NICKEL FILTER, $\lambda = 1.5418$Å

California			Malhada do Angico, Brazil	
d/n	I	hkl	d/n	I
—			13.7	½
—			12.6	½
9.75	½	011	10.9	1
7.13	½	020	7.10	1
5.98	1	002	5.90	1
4.76	½	031	4.68	1
4.58	½	131	—	
4.06	1	003, 222, 231	4.00	2
3.76	½	113	—	
3.52	1	023, 232, 240	3.45	2
3.27	½ b	042	3.23	1
3.02	½	051, 242, 341	—	
2.96	3	004, 151	2.94	4
2.78	10	440, 024, 052	2.74	10
—			2.65	½
2.61	10	060, 252, 224	2.58	8
—			2.52	½
2.47	3	261, 234, 343	2.44	7
2.365	1	005, 044, 144, 162	2.36	1
—			2.33	1
2.297	½	262	—	
2.25	½	025, 125, 170, 443	2.26	½
—			2.224	½
—			2.19	2
2.14	2	035, 135, 163	2.12	3
2.088	½	172, 235	—	
2.074	½	254, 552	2.075	½
—			2.06	½
2.01	½	145	2.03	½
1.97	½	066, 064, 164	1.995	1
—			1.955	1
1.91	2 b	026, 293, 562	1.916	1
—			1.876	2
1.806	½	236, 445	1.820	½
1.778	1	554	1.788	½
—			1.756	2
1.726	½	191, 246	—	
1.69	2	291, 482, 660	1.711	½
1.671	3	192, 564, 573	1.673	1
1.634	9	007	1.658	3
—			1.618	8
1.567	2	237	1.564	½
—			1.556	1
—			1.534	½
—			1.519	½
1.510	½		1.505	½
—			1.493	1
1.482	½		—	

Å. Space group D_{4h}^4,$P4/nnc$. These values agree closely with the elements derived from goniometric measurements, and for a represent a value considerably higher than previously reported.

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