

Crystal structure of a REE-bearing vesuvianite from San Benito County, California

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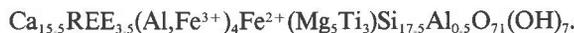
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ABSTRACT

The crystal structure of a REE-bearing vesuvianite from San Benito County, California, was determined using single-crystal X-ray diffraction methods. The sample with tetragonal space group $P4/n$ has cell parameters of $a = 15.799(3)$ and $c = 11.917(3)$ Å. An R value of 6.64% was reached for 2874 unique reflections with $|F_o| > 3\sigma_{|F_o|}$.

This vesuvianite shows complex coupled substitution in accommodating the REE: (1) REEs substitute for Ca, (2) Ti substitutes for Al in the general Al-Fe site, (3) O(11) bridging the REE and Ti is oxygen, unlike in other vesuvianites in which it is hydroxyl, (4) Mg substitutes for Al in the Al-Fe site to maintain overall charge neutrality.

The formula for this vesuvianite is ideally



INTRODUCTION

A REE-bearing vesuvianite from San Benito County, California, was described in 1966 by Murdoch and Ingram, who reported 16.7 wt% REE, the greatest amount known in any vesuvianite. This study examines the atomic structure and crystal chemistry of a crystal from the same locality.

EXPERIMENTAL DETAILS

The crystal used in this study is a black single crystal (no. 125012) from the collection of the U.S. National Museum. The sample was analyzed using an ARL-SEM-Q electron microprobe at an operating voltage of 15 kV and a beam current of 0.15 μA . The data were corrected using the Modified Magic IV program. The standards used were hornblende (Si, Al, Fe, Mg, K, Ti, Na), wollastonite glass (Ca), apatite (F), gahnite (Zn), manganite (Mn), copper oxide (Cu), and Drake REE glasses (REE). REE were also corrected for overlap, with overlap percentages determined experimentally using pure phosphates of the individual elements. Estimated precision of the individual oxide values is 3–4% for all elements. Water was calculated from the structural determination. The chemical analysis of this vesuvianite is similar to that of Murdoch and Ingram and is given in Table 1. The formula will be discussed in a later section.

This sample was mounted on a fine glass fiber. Table 2 gives the unit-cell parameters obtained from the least-squares fit of the angular settings of 25 reflections, $23^\circ \leq 2\theta \leq 33^\circ$. Numerous violations to extinction criteria of the second and third glide

planes for $P4/nnc$ were present, and refinement was carried out in $P4/n$ with the atomic coordinates of vesuvianite from Asbestos, Quebec, used as a starting model (Fitzgerald et al., 1986b).

The assignment of elements to atomic positions was complicated by the complex chemistry of this vesuvianite. Site assignments and terminology were based on the model of Rucklidge et al. (1975). Difference Fourier electron-density peaks immediately indicated the position of the REE atoms in the Ca(3)

TABLE 1. Electron-microprobe data of San Benito County vesuvianite

Oxide	Wt%	REE oxide	Wt%
CaO	26.02	Ce ₂ O ₃	9.88
K ₂ O	0.04	La ₂ O ₃	5.58
Na ₂ O	0.06	Nd ₂ O ₃	1.23
Al ₂ O ₃	4.35	Pr ₂ O ₃	0.28
MgO	4.75	Gd ₂ O ₃	0.15
TiO ₂	6.69	Sm ₂ O ₃	0.07
ZnO	0.44		17.19
MnO	0.37		
FeO	6.56		
CuO	0.34		
REE	17.19		
SiO ₂	30.55		
F	0.18		
H ₂ O (calc.)	1.93		
	99.47		
–O = F	0.08		
	99.39		

TABLE 2. Crystal and structure-refinement data at 22°C

Crystal system	tetragonal
Space group	<i>P4/n</i>
<i>a</i> (Å)	15.799(3)
<i>c</i> (Å)	11.917(3)
<i>V</i> (Å ³)	2974.5
<i>Z</i>	2
Color	black
Crystal size	0.256 × 0.3 mm prism
Radiation	graphite-monochromatized MoK α
Diffractometer	Nicolet R3
μ_1 (cm ⁻¹)	58.57
Scan speed (°/min)	var 4–20
2 θ scan range (°)	4.0 < 2 θ < 55.0
Scan technique	omega
Data collected	+ <i>h</i> , + <i>k</i> , + <i>l</i>
Scan width (°)	0.8 ± $\Delta(\alpha_1, -\alpha_2)$
Weighting factor <i>g</i> *	0.00085
Unique reflections	3426
Unique data with (<i>F</i> _o) > 3 σ (<i>F</i> _c)	2874
Standard reflections	3/197
Parameters refined	197
Data/parameter ratio	14.6
<i>R</i> %(<i>F</i> _o)	6.64
<i>R</i> _w %(<i>F</i> _o)	7.22

* $w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

sites. Ce, the single most abundant REE in the sample, was chosen to represent all the REEs in the refinement. The occupancy factors for the two Ca(3)-Ce(3) sites refined to different values with Ca(3a) = 0.64 and Ce(3a) = 0.42, giving a total of greater than 1.0. Ca(3b) = 0.31 and Ce(3b) = 0.51 refined to a total occupancy of less than 1.0, suggesting that the REEs do not occupy the Ca(3) sites equally. Ca was also assigned to the C site. Al was assigned to the A site, but the occupancy was allowed to vary during the refinement as the amount of Al in the structure was not sufficient to fill this position totally.

Mg and Fe were used to represent an average for Mg, Ti, Mn, Fe, and Zn in the general Al-Fe site. Fe was assigned to the B site. Occupancies were refined for the C and B sites. The ratio of the occupancies found for the Ca(C1) and Fe(B1) to Ca(C2) and Fe(B2) is 2 to 1; however, for final refinement the constraints of Ca(C1) = Ca(C2) and Fe(B1) = Fe(B2) were made. Atomic coordinates are given in Table 3 and anisotropic thermal parameters in Table 4. A final *R* of 6.64% was reached for this structure.

DISCUSSION

The abundance of REEs, the low content of Al, the high content of Mg and Ti, and the unusual site distribution of elements differentiate this vesuvianite from others.

The three Si positions contain only Si and minor amounts of Al, and the Ca positions contain both Ca and the REEs. The REEs found in this vesuvianite are, in decreasing order of abundance, Ce, La, Nd, Pr, Gd, and Sm.

Calculation of the formula on the basis of 50 cations gives 3.51 REE cations or 44% of the Ca(3) sites, in good agreement with the occupancies determined by the structural analysis.

The C site contains Ca, and the A site, which contains only Al in other analyzed vesuvianites, contains both Al and Fe in this vesuvianite. The 2.17 atoms of Al and

TABLE 3. Atomic coordinates (×10⁴) and temperature factors (Å² × 10³) for San Benito County vesuvianite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} *
Si(1a)	-¼	¼	½	8(1)
Si(1b)	-¼	¼	0	10(1)
Si(2a)	-404(2)	3187(2)	1279(2)	10(1)
Si(2b)	-408(2)	1812(1)	3726(2)	12(1)
Si(3a)	848(2)	1507(2)	6375(2)	10(1)
Si(3b)	851(2)	3489(2)	-1371(2)	10(1)
Ca(1a)	-¼	¼	2496(3)	14(1)
Ca(2a)	1893(1)	-477(1)	6219(2)	12(1)
Ca(2b)	-474(1)	1893(1)	-1220(2)	13(1)
Ca(3a)	1784(1)	3985(1)	1094(1)	14
Ce(3a)	1784(1)	3985(1)	1094(1)	12(1)
Ca(3b)	3219(1)	3988(1)	-6087(1)	14
Ce(3b)	3219(1)	3988(1)	-6087(1)	13(1)
Ca(c1)	¼	¼	-3530(8)	33(2)
Ca(c2)	¼	¼	-1453(8)	15(2)
Mg(1a)	2(1)	-1108(1)	1197(2)	14
Fe(1a)	2(1)	-1108(1)	1197(2)	5(1)
Mg(1b)	-1204(1)	1114(1)	6266(2)	14
Fe(1b)	-1204(1)	1114(1)	6266(2)	7(1)
Ala(1)	0	0	½	18(1)
Ala(2)	0	½	0	23(1)
Feb(1)	¼	¼	-511(7)	19(2)
Feb(2)	¼	¼	-4574(6)	22(2)
O(1a)	-2245(4)	1739(4)	852(6)	12(2)
O(1b)	-2786(5)	1731(4)	4143(6)	15(2)
O(2a)	-1171(5)	1626(4)	2821(6)	14(2)
O(2b)	-1169(5)	3372(4)	2183(6)	14(2)
O(3a)	-448(4)	2244(4)	710(6)	13(2)
O(3b)	-469(4)	2767(4)	4264(6)	12(2)
O(4a)	-594(4)	1045(4)	4690(6)	12(2)
O(4b)	-592(4)	3925(4)	330(6)	12(2)
O(5a)	-87(4)	3272(4)	-1805(6)	14(2)
O(5b)	-103(4)	1723(4)	6797(6)	14(2)
O(6a)	1209(5)	2755(5)	-584(7)	20(2)
O(6b)	1225(4)	2224(5)	5534(6)	17(2)
O(7a)	554(4)	1757(5)	3227(7)	16(2)
O(7b)	573(4)	3242(4)	1777(6)	15(2)
O(8a)	937(5)	4390(5)	-733(6)	14(2)
O(8b)	953(4)	594(4)	5730(6)	13(2)
O(9a)	1474(4)	1475(4)	7500(6)	14(2)
O(10a)	¼	¼	1397(18)	37(5)
O(10b)	-¼	-¼	-3603(21)	36(6)
O(11a)	-19(4)	630(5)	1366(7)	16(2)
O(11b)	-625(4)	11(4)	6352(6)	15(2)

Note: Estimated standard deviations (esd's) are in parentheses.

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_i tensor.

1.83 atoms of Fe³⁺ for this site fit well with the occupancy factor and with bond-length considerations (Table 5).

The general Al-Fe site in this vesuvianite contains Mg, Ti, Mn, Fe, and Zn, with Mg the dominant element rather than the usual Al. Although Mg and Fe were refined in this site to represent average scattering factors, there is a substantial amount of Ti in this site as well as Fe and minor amounts of Mn and Zn. The occupancy factor is compatible with the inferred atomic content in this site. The larger ionic size of Mg and Ti is reflected in a slightly longer bond length in this vesuvianite in comparison to others that have predominately Al in this site (Fitzgerald et al., 1986b).

The B site contains Fe and minor amounts of Cu, assigned on the basis of the structure of cuprian vesuvianite (Fitzgerald et al., 1986a). Although the B-O(10) bond

TABLE 4. Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$) for San Benito County vesuvianite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1a)	8(1)	8(1)	4(2)	0	0	0
Si(1b)	8(1)	8(1)	15(3)	0	0	0
Si(2a)	14(1)	9(1)	8(1)	0(1)	1(1)	-1(1)
Si(2b)	11(1)	11(1)	15(1)	-0(1)	-2(1)	-1(1)
Si(3a)	12(1)	8(1)	11(1)	-0(1)	-1(1)	0(1)
Si(3b)	11(1)	10(1)	8(1)	0(1)	-0(1)	-2(1)
Ca(1a)	21(1)	13(1)	10(1)	0	0	-0(1)
Ca(2a)	11(1)	13(1)	14(1)	-0(1)	-1(1)	0(1)
Ca(2b)	14(1)	11(1)	13(1)	1(1)	-0(1)	2(1)
Ce(3a)	9(1)	12(1)	16(1)	3(1)	0(1)	5(1)
Ce(3b)	10(1)	14(1)	16(1)	-2(1)	-0(1)	5(1)
Ca(1)	38(2)	38(2)	21(5)	0	0	0
Ca(2)	15(2)	15(2)	17(4)	0	0	0
Fe(1a)	9(2)	2(2)	3(2)	-2(2)	2(2)	2(2)
Fe(1b)	8(2)	7(2)	8(2)	-3(2)	-1(2)	-5(2)
Ala(1)	19(2)	17(2)	19(2)	-1(1)	-1(1)	-0(1)
Ala(2)	18(2)	18(2)	32(2)	-0(2)	4(2)	-1(1)
Feb(1)	12(2)	12(2)	33(4)	0	0	0
Feb(2)	18(2)	18(2)	30(4)	0	0	0
O(1a)	16(3)	10(3)	9(3)	4(3)	-1(3)	-3(3)
O(1b)	21(4)	9(3)	14(4)	5(3)	2(3)	-0(3)
O(2a)	18(4)	8(3)	17(4)	-0(3)	-4(3)	2(3)
O(2b)	12(3)	13(3)	16(4)	-2(3)	1(3)	-3(3)
O(3a)	13(3)	11(3)	15(4)	-7(3)	-1(3)	4(3)
O(3b)	12(3)	12(3)	12(4)	2(3)	3(3)	3(3)
O(4a)	13(3)	14(3)	8(3)	0(3)	-2(3)	4(3)
O(4b)	17(3)	8(3)	11(3)	3(3)	-2(3)	1(3)
O(5a)	11(3)	18(4)	13(4)	-6(3)	-1(3)	-6(3)
O(5b)	16(4)	13(3)	14(4)	-1(3)	-4(3)	2(3)
O(6a)	25(4)	19(4)	17(4)	10(3)	0(3)	3(3)
O(6b)	15(4)	22(4)	15(4)	-7(3)	-3(3)	2(3)
O(7a)	10(3)	15(4)	22(4)	-2(3)	-1(3)	1(3)
O(7b)	16(4)	16(4)	13(4)	-2(3)	-3(3)	-1(3)
O(8a)	14(4)	17(4)	12(4)	0(3)	6(3)	1(3)
O(8b)	18(4)	4(3)	16(4)	-4(3)	2(3)	1(3)
O(9a)	16(3)	13(3)	12(3)	-2(3)	-0(3)	-2(3)
O(10a)	27(5)	27(5)	57(13)	0	0	0
O(10b)	22(6)	22(6)	62(16)	0	0	0
O(11a)	15(4)	15(4)	20(4)	2(3)	-2(3)	-3(3)
O(11b)	13(2)	18(4)	13(4)	2(3)	-0(3)	2(3)

Note: The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2hka^*b^*U_{12})$. Esd's are in parentheses.

TABLE 5. Interatomic distances (\AA) in cation-coordination polyhedra

Si(1)-O(1)	1.650(7)	Ca(3)-O(3)	2.446(7)
	1.625(7)		2.480(7)
Mean	1.638	-O(6)	2.934(8)
			2.514(8)
Si(2)-O(2)	1.645(8)	-O(7)	2.644(8)
	1.644(8)		2.639(7)
-O(3)	1.643(7)	-O(7)	2.555(7)
	1.638(7)		2.540(7)
-O(4)	1.651(7)	-O(7)	2.388(7)
	1.696(7)		2.410(7)
-O(7)	1.635(8)	-O(8)	2.635(8)
	1.655(8)		2.614(7)
Mean	1.651	-O(10)	2.630(3)
			2.638(4)
Si(3)-O(5)	1.621(8)	-O(11)	2.469(7)
	1.608(7)		2.458(7)
-O(6)	1.625(8)	Mean	2.578
	1.595(8)		
-O(8)	1.643(7)	C-O(6)	2.343(9)
	1.620(8)		2.323(9)
-O(9)	1.666(8)	-O(9)	2.599(9)
	1.669(8)		2.609(9)
Mean	1.631	Mean	2.469
Ca(1)-O(1)	2.334(7)	B-O(6)	2.081(8)
	2.351(8)		2.065(7)
-O(2)	2.542(7)	-O(10)	2.173(26)
	2.543(7)		2.274(23)
Mean	2.443	Mean	2.103
Ca(2)-O(1)	2.543(7)	Al-Fe-O(1)	2.053(7)
	2.471(7)		1.987(8)
-O(2)	2.429(7)	-O(2)	1.967(8)
	2.439(7)		1.967(8)
-O(3)	2.366(7)	-O(3)	2.068(7)
	2.391(7)		2.020(7)
-O(4)	2.487(7)	-O(4)	2.138(7)
	2.500(7)		2.114(7)
-O(5)	2.368(7)	-O(5)	2.106(7)
	2.367(7)		2.085(7)
	2.450(7)	-O(11)	1.944(8)
	2.448(7)		1.970(7)
-O(8)	2.325(7)	Mean	2.035
	2.355(8)		
Mean	2.424	A-O(4)	1.934(7)
			1.979(6)
		-O(8)	1.977(7)
			1.971(7)
		-O(11)	1.890(7)
			1.908(8)
		Mean	1.943

length is longer than the B-O(6) bond length, the degree of distortion in minor.

Bond-strength calculations suggest that O(10) is always a hydroxyl in the San Benito vesuvianite. If the B site is not occupied, the bond strength is 1.1 (Donnay and Allman, 1970). If the B site is occupied, the bond strength is 1.3 for Fe²⁺ occupation and 1.4 for Fe³⁺ occupation. Charge balance would be more favorable if Fe²⁺ occupied the B site, and crystal-field considerations also suggest that Fe²⁺ is more likely than Fe³⁺ to occupy such a distorted site (Burns, 1970).

The case for O(11) is more complex. In other vesuvianites that have been structurally analyzed, O(11) is entirely a hydroxyl. In the San Benito vesuvianite, some O(11) must be oxygen to compensate for the higher total charge introduced by the presence of the REEs. O(11) is bonded to one Ca(3), one Al-Fe and one A. If Ca(3) is occupied by Ca and Al-Fe by Mg, the bond strength is

1.2 and O(11) is a hydroxyl. If, however, Ca(3) is occupied by the REEs and Al-Fe by Ti, then the bond strength is 1.9 and O(11) is an oxygen. With about three atoms of Ti in the formula, three of eight O(11)'s are oxygens. The bond-strength calculations provide a strong argument that REEs and Ti are bonded to the same O(11)'s and that Ca and Mg are bonded to the same OH(11)'s. This pattern can be considered a coupled substitution of the REEs and of Ti for Ca and Mg. This pattern may occur in other REE-bearing vesuvianites. In addition, Mg substitutes for Al in the general site to maintain overall charge balance.

This model does not account for all the REE. Three atoms of REE can be accommodated, at which occupancy the general site is filled with Mg and Ti at the expense of Al, which dominates the site in other vesuvianites. However, both the structural refinement and the chemical analysis suggest 3.5 atoms of REEs in the San Benito

vesuvianite. The excess 0.5 atoms of REE may be balanced by substitution of Al for Si or by the conversion of another 0.5 atom of O(11) from hydroxyl to oxygen. Both mechanisms are compatible with the chemical analysis. Based on a total of 50 cations, the following formula can be written for the San Benito vesuvianite: $(\text{Ca}_{15.78}\text{-REE}_{3.51})_{\Sigma=19.29}(\text{Al}_{2.17}\text{Fe}_{1.83})_{\Sigma=4}(\text{Fe}_{0.86}\text{Cu}_{0.14})(\text{Mg}_{4.01}\text{Ti}_{2.86}\text{Fe}_{0.41}\text{Mn}_{0.17}\text{Zn}_{0.17})_{\Sigma=7.62}(\text{Si}_{17.28}\text{Al}_{0.72})\text{O}_{70.4}(\text{OH},\text{F})_{7.6}$ or ideally $(\text{Ca}_{15.5}\text{-REE}_{3.5})(\text{Al},\text{Fe}^{3+})_4(\text{Fe}^{2+})(\text{Mg}_5\text{Ti}_3)\text{Si}_{17.5}\text{Al}_{0.5}\text{O}_{71}(\text{OH})_7$.

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