Cerite, $RE_9(Fe^{3+},Mg)(SiO_4)_6(SiO_3OH)(OH)_3$: its crystal structure and relation to whitlockite

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Abstract

Cerite, $(Ce,La,Nd,Ca)_9(Fe^{3+},Mg,Al)(SiO_4)_6(SiO_3OH)(OH)_3$, rhombohedral, $a = 10.779(6)$, $c = 38.061(7)$Å, $Z = 6$, space group $R3c$, is nearly isostructural to whitlockite, $Ca_9Mg(PO_4)_6(PO_3OH)$. $R = 0.032$ for 1711 independent reflections.

Cerite is related to a large family of "bracelet and pinwheel" structures derived from glaserite, $KNa_3(SO_4)_2$. Rods of two kinds run parallel to the c-axis. One rod is partly disordered at $(00z)$ and includes the (SiO_3OH) tetrahedron and $(OH)^-$ groups, the latter bonded to the RE ions. The other rod at (x,y,z) which is fully occupied is based on the corner-, edge-, and face-linkages of $Si(1)O_4$ and $Si(2)O_4$ tetrahedra and $RE(1)O_8OH$, $RE(2)O_8OH$ and $RE(3)O_8OH$ polyhedra. Omitting the bond to OH, the anhydrous REO_8 group is a polyhedron of order 8 and has maximal point symmetry $D2d$. The OH^- ligands bond through a rhombus-shaped window in this polyhedron. Average distances are $^{[9]}RE(1)-O = 2.59$, $^{[9]}RE(2)-O = 2.55$, $^{[9]}RE(3)-O = 2.59$, $^{[6]}(Mg,Fe^{3+},Al)-O = 2.07$, $^{[4]}Si(1)-O = 1.63$ and $^{[4]}Si(2)-O = 1.63$Å.

It is suggested that cerite probably has F^- analogues, and is related to a substantial family of rare earth silicates with rhombohedral structures such as cappelenite, okanoganite and steenstrupine.

Introduction

Cerite, a silicate of the rare earths (=RE), was first named and described by Jöns Jacob Berzelius. The mineral from the Bastnäs Mine, Riddarhyttan, Sweden, provided Berzelius and his students with a source for several new rare earth elements, including cerium (Jorpes, 1966).

Cerite has been suspected to be isostructural with whitlockite, $Ca_9Mg(PO_4)_6(PO_3OH)$, just as beckelite, $Ca_2RE_3(SiO_4)_3(OH)$ is isostructural with apatite, $Ca_2Ca_3(PO_4)_3(OH)$. In addition, törnebohmite, $RE_2Al(OH)(SiO_4)_2$, which occurs with cerite at the type locality, is found to be isostructural with fornacite, $Pb_2Cu(OH)(AsO_4)(CrO_4)$ (Shen and Moore, 1982). Therefore, a structure study of cerite seemed highly desirable. In addition, a suspected kinship with equally complex RE silicates okanoganite, cappelenite and steenstrupine warranted the investigation.

Experimental procedure

Cerites from several sources were studied. We thank Messrs. John S. White, Jr. and Pete J. Dunn, U.S. National Museum of Natural History, Smithsonian Institution for cerite from Bastnäs, Sweden (USNM R3925) and Mountain Pass, San Bernardino County, California (USNM 117769); Dr. Carl A. Francis of Harvard Mineralogical Museum for Riddarhyttan, Sweden material (HMM 86268); and Dr. John W. Adams of Lakewood, Colorado for a related material from Jamestown, Colorado. The chemical investigation by Glass *et al.* (1958) suggested that Mountain Pass material would be more appropriate for study than Bastnäs material. Dr. Howard T. Evans, Jr. traced this original sample studied by Glass *et al.* to the Smithsonian specimen. A nearly equant grain measuring $0.09 \times 0.11 \times 0.12$ mm from Mountain Pass, California was selected for the ensuing study.

Precession photographs indicated good quality of the

crystal, and extinctions compatible with space group $R3c$, which is confirmed by the refinement of the structure. The crystal data were collected on a Picker FACS-1 diffractometer with MoK_α ($\lambda = 0.70926$Å) radiation. Cell parameters refined on this instrument led to $a = 10.779(6)$, $c = 38.061(7)$Å. With reflections to $2\theta = 65°$, scan speed $2°$ min^{-1}, base scan widths of $2°$ and background counting time of 20 sec on each side of the peak, a total of 7262 reflections was collected. No absorption correction was applied, despite the relatively high linear atomic absorption coefficient of about 131.70 cm^{-1}, due to the absence of regular crystal faces, the approximately equant, isometric crystal shape and similar intensities among equivalent reflections. From three to six equivalent reflections were averaged to obtain the independent reflections. Caution should be applied to the refined temperature factors since no absorption correction was made. After Lorentz-polarization correction, a total of 1711 independent $|F_o|$ was obtained. The hexagonal coordinate system was adopted throughout this study.

Statistical tests indicated a centrosymmetric structure. However, we had already noted a close correspondence between cerite and whitlockite, and decided to explore the possibility of isomorphism, $viz.$ the whitlockite data obtained from Calvo and Gopal (1975).

	Cerite	Whitlockite
a(Å)	10.78	10.33
c(Å)	38.06	37.10
S.G.	$R3c$	$R3c$
Formula	$(RE,Ca)_9(Fe,Mg,Al)(SiO_4)_6(SiO_3OH)(OH)_3$	
	$Ca_9Mg(PO_4)_6(PO_3OH)\square_3$,	
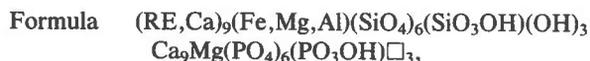
Solution and refinement of the structure

Conclusions regarding interpretation of Mountain Pass cerite's chemistry were not made until appropriate convergence of the structure refinement. Since the rule for isomorphism appeared to be $RE^{3+}Si^{4+} \leftrightarrows Ca^{2+} P^{5+}$, we initiated the structure analysis by transferring coordinates of Ca, Mg, P and O in whitlockite to Re, Mg, Si and O in cerite. At this stage, the role of C was uncertain for Mountain Pass cerite, and we suspected its presence would be indicated by short O–O distances (2.2–2.4Å) consistent with CO_3 groups or such short distances would be absent in the structure, in which case the $(CO_3)^{2-}$ group reported in the chemical analysis would be an impurity ion. Site occupancy parameters for the large cations (REE) and, subsequently, the disordered atoms at 00z were allowed to vary yielding $R = 0.23$. Addition of ten non-equivalent oxygens led to $R = 0.17$.

A Fourier electron density map and subsequent difference Fourier synthesis revealed substantial residues along the 00z rod. At this stage, and at any subsequent stage of analysis, we failed to find any evidence for $(CO_3)^{2-}$ groups. We assumed these residues were in fact the water molecules reported in the chemical analysis. In addition, a partly disordered (SiO_3OH) group, like the (PO_3OH) group along 00z in whitlockite, was assumed. A sequence of site population and atomic coordinate refinements, followed by difference Fourier syntheses, led to $R = 0.095$. Anisotropic refinement for all atoms associated with rod II at xyz and subsequent full-matrix refinement (excepting anisotropic thermal parameters along 00z) led to $R = 0.032$ for all 1711 independent reflections where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}.$$

The final cycle included 170 variable parameters, giving a variable parameter to data ratio of 10:1. The SHELX-76 program system was used at the VAX computer facility of The University of Chicago. Scattering curves for Ce^{3+}, Mg^{2+}, Si^{4+} and O^{1-} were obtained from $International$ $Tables, vol. 4$ (1974) and anomalous dispersion correction, f'', for all metals from Cromer and Liberman (1970). Atomic coordinate and anisotropic thermal vibration parameters are given in Table 1, structure factor tables in Table 2[1] and bond distances and angles in Table 3.

From the site population refinements in Table 1, it appears that all large cation sites are occupied by more than one type of atom. The apparent site populations of less than unity (relative to the Ce^{3+} scattering curve) indicate the presence of an additional element of lower atomic number, which can be identified as Ca^{2+} on the basis of the chemical analysis (Table 5). Slightly decreasing site populations from RE(1) to RE(3) suggest that principally rare earths, and a lower Ca^{2+} content, occur at RE(1), with increasing Ca^{2+} at the subsequent two sites. Since La, Ce and Nd are the principal rare earths in Mountain Pass cerite according to Glass et $al.$ (1958), the light rare earths evidently predominate in our sample.

Description of the structure

Cerite is based on the same structural principle as whitlockite. The whitlockite structure was reported by Calvo and Gopal (1975) and was treated as a glaserite-related rod packing by Moore (1981). In the present study, the atomic sites of Calvo and Gopal were assigned simpler labels. The underlying features of the structures are two distinct rods, rod I at (00z) and rod II centered at $ca.$ ($\frac{1}{3}\frac{1}{6}z$); the remaining rod locations in the cell are determined by the space group $R3c$. For convenience, these rods will be treated separately, then integrated to define the structure. Rod II in particular defines a pinwheel-type arrangement with circumjacent linkages by (SiO_4) tetrahedra. The unit fragment of rod II is featured in Figure 1.

Table 1. Cerite: atomic coordinate and anisotropic thermal vibration ($\times 10^4$) parameters†

	K	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
RE(1)	0.940(5)	0.2552(1)	0.1318(1)	0.0683(2)	120(13)	110(3)	98(3)	-2(3)	17(2)	72(3)
RE(2)	0.890(5)	0.1435(1)	0.2621(1)	0.4329(2)	111(4)	294(5)	158(3)	127(3)	52(4)	125(4)
RE(3)	0.879(5)	0.2592(1)	0.1357(1)	0.1762(2)	160(4)	146(4)	112(3)	-41(3)	-37(2)	107(3)
Si(1)	1	0.3164(4)	0.1471(4)	0.3641(2)	83(13)	125(14)	128(14)	1(12)	4(10)	71(12)
O(1)	1	0.2653(14)	0.0907(15)	0.3232(3)	325(50)	493(60)	247(46)	-158(45)	-127(41)	254(46)
O(2)	1	0.2764(9)	0.0034(9)	0.3871(3)	91(33)	117(34)	184(35)	-11(29)	13(29)	38(28)
O(3)	1	0.2578(12)	0.2478(12)	0.3796(3)	239(41)	228(40)	220(43)	17(33)	45(34)	227(35)
O(4)	1	0.0857(10)	0.1785(10)	0.0334(3)	121(34)	100(33)	244(40)	-47(32)	43(33)	44(29)
Si(2)	1	0.1499(4)	0.3255(5)	0.1376(2)	93(13)	120(14)	115(12)	1(10)	-5(13)	3(13)
O(5)	1	0.2415(11)	0.2645(11)	0.1177(3)	151(36)	175(38)	115(35)	-70(30)	-25(29)	41(31)
O(6)	1	-0.0140(10)	0.2640(10)	0.1236(3)	140(36)	197(39)	110(32)	10(30)	-26(28)	57(31)
O(7)	1	0.1682(9)	0.0743(10)	0.4655(3)	50(31)	64(31)	362(46)	9(33)	-48(31)	15(26)
O(8)	1	0.1396(10)	0.2824(9)	0.1788(2)	128(33)	176(35)	41(29)	3(26)	29(28)	79(30)
M	1.460(8)	0.0000	0.0000	0.0000	138(79)	126(79)	108(20)	51(93)	-66(92)	-16(80)
Si(c)	0.862(7)	0.0000	0.0000	0.2524(2)	133(17)	133	61(23)	0	0	67(9)
O(9)	1	0.1602(11)	0.0392(12)	0.2398(3)	150(37)	370(50)	192(38)	-39(36)	-35(32)	129(36)
OH	0.866(9)	0.0000	0.0000	0.2967(5)	311(56)	311	148(67)	0	0	155(28)
OH(1a)	0.097(8)	0.0000	0.0000	0.0638(37)	224(100)	224	80(101)	0	0	112(50)
OH(1)	1	0.0000	0.0000	0.0900(5)	59(33)	59	290(62)	0	0	30(17)
OH(3)	0.936(9)	0.0000	0.0000	0.1633(5)	112(38)	112	210(59)	0	0	56(19)
Ca(x)	0.169(9)	0.0000	0.0000	0.3444(13)	251(81)	251	329(92)	0	0	125(40)
OH(2)	1	0.0000	0.0000	0.4090(5)	275(49)	275	208(64)	0	0	137(24)

†Estimated standard errors refer to the last digit. K, the site multiplicity, was based on Ce^{3+} for RE, Mg^{2+} for M, Si^{4+} for Si(c), Ca^{2+} for Ca(x) and O^{1-} for the oxygens. The anisotropic thermal vibration parameters are coefficients in the expression $\exp-[U_{11}h^2 + U_{22}k^2 + U_{33}\ell^2 + 2U_{12}hk + 2U_{13}h\ell + 2U_{23}k\ell]$.

The most intriguing feature of rod II is the oxygen coordination polyhedra about the RE cations. If we disregard the RE–O bonds to anions along rod I, a direct comparison to whitlockite can be made. RE(1), RE(2) and RE(3) are in fact the same kind of polyhedra. Ideally, this is polyhedron No. 14 in Britton and Dunitz (9173) which we shall call the *D2d dodecahedron*. It is one of 257 nonisomorphic polyhedra of order 8, and has $N_0 = 8$ vertices, $N_1 = 18$ edges and $N_2 = 12$ facets. Constructed of twelve regular triangles, it is a convex polyhedron, with point symmetry $D2d$ ($\bar{4}m2$). In Figure 1, the loci of the 2-fold component of the pseudo-$\bar{4}$ axes for the three successive $D2d$ dodecahedra are presented. The central RE(3)O_8 polyhedron shares two edges with RE(2) and RE(1) above and below. In addition, two more edges for RE(3) are shared with RE(2), defining a shared face. In both the cerite and whitlockite structures, the components of rod II appear to be the underlying basis of the structure's stability and there is no evidence of disorder in this region.

The situation is quite different for rod I, which appears to be a more variable part of the structure. An excellent survey of the whitlockite crystal chemistry was offered by Calvo and Gopal (1975). As amplified by Moore (1981), the structure is based on a rod packing over the $\{6\cdot3\cdot6\cdot3\}^4$ Kagomé net. Rods of type II occur at the nodes of the net, and rods of type I occur at the centers of the hexagons. Since the ratio of centers to nodes in the $\{6^3\}$ net is 1:2, this means that the ratio of rod I:rod II = 1:3. An outline of the contents along the rod I axis at $(00z)$ is presented in Table 4, derived from the asymmetric unit contents in Table 1. Here, the coordinate free variable (z) and the cell

population from refinement are listed for both whitlockite (Calvo and Gopal, 1975) and cerite. Frondel (1949) lists 11 chemical components in Palermo whitlockite; of these, only 6 are in amounts greater than 0.5 wt.%. Calvo and Gopal have shown that 4 are essential. The analysis of Glass *et al.* (1958) (Table 5) suggests 10 components in amounts greater than 0.5 wt.%, with Ce_2O_3 and the La_2O_3 rare earths treated separately. The components in Table 5 have been grouped according to ionic radius. No evidence of $(CO_3)^{2-}$ groups was found in our study. Therefore, we assumed all CO_2 reported in the analysis was a contaminant, specifically bastnäsite. Subtracting 17.7% $CeLaF_2(CO_3)_2$ led to column 2, which still possesses a relatively large number of components, namely 8. From this total, cation contents in the cell were calculated from our cell parameters and Glass *et al.*'s specific gravity. Clearly the problem rests with the M site, where five cations could play some role. In addition, about 5.5 H atoms reside in the formula unit (Z = 6), either bound as OH^- groups, neutral water molecules (H_2O), hydronium ions (H_3O^+), or any combination of these.

Column 4 is particularly instructive. The sum of large cations closely matches the theoretical limit for complete cation occupancy in rod II. The octahedral cations total to 1.55, in contrast with 1.00 for the theoretical limit. This could mean either the presence of impurities or additional occupied sites along rod I. The tetrahedral species sum to 6.79, where 6.00 cations would constitute fully occupied tetrahedra in rod II, and 0.79 would be the tetrahedral fraction in rod I. The tetrahedral occupancy for Si(c) refined to 0.86 at this site. The analysis and the assumptions made by Glass *et al.* seem to be valid, with excellent

Table 3. Cerite: bond distances and angles†

RE(1)

RE(1)-O(5)	2.411(7) Å	
-O(8)$^{(9)}$	2.455(7)	
-O(4)$^{(2)}$	2.494(7)	
-O(4)	2.505(7)	
-O(6)$^{(2)}$	2.533(7)	
-O(2)$^{(13)}$	2.629(7)	
-O(3)$^{(14)}$	2.824(7)	
-O(9)$^{(11)}$	2.906(7)	
Average	2.595 Å	

Si(1)		O(2)$^{(13)}$-O(4)$^{(2)}$	2.55(2)	59.7(3)°
Si(1)	r	O(3)$^{(14)}$-O(4)	2.58(2)	57.3(3)
		O(3)$^{(11)}$-O(9)$^{(11)}$	2.81(2)	58.7(3)
M		O(4)-O(4)$^{(2)}$	2.89(2)	70.5(3)
	r	O(2)$^{(13)}$-O(6)$^{(2)}$	2.91(2)	68.6(3)
RE(3)		O(5)-O(6)$^{(2)}$	2.92(2)	72.5(3)
		O(2)$^{(13)}$-O(8)$^{(9)}$	2.96(2)	71.1(3)
	m	O(8)$^{(9)}$-O(9)$^{(11)}$	2.97(2)	66.6(3)
		O(3)$^{(14)}$-O(8)$^{(9)}$	3.00(2)	68.9(3)
		O(3)$^{(14)}$-O(5)	3.18(2)	70.5(3)
	m	O(4)$^{(2)}$-O(8)$^{(9)}$	3.18(2)	80.1(3)
		O(4)-O(8)$^{(9)}$	3.24(2)	81.6(3)
	m	O(5)-O(9)$^{(11)}$	3.34(2)	77.2(3)
		O(4)-O(5)	3.52(2)	91.6(4)
		O(4)$^{(2)}$-O(6)$^{(2)}$	3.84(3)	99.8(4)
		O(6)$^{(2)}$-O(9)$^{(11)}$	3.97(3)	93.6(4)
		O(2)$^{(13)}$-O(9)$^{(11)}$	4.11(3)	95.7(4)
	m	O(4)$^{(2)}$-O(5)	4.59(4)	138.6(5)
		Average	3.25	79.0

RE(2)$^{(9)}$

RE(2)$^{(9)}$-O(2)$^{(11)}$	2.397(7)	
-O(3)$^{(9)}$	2.421(7)	
-O(7)$^{(11)}$	2.465(7)	
-O(7)$^{(9)}$	2.496(7)	
-O(9)	2.513(7)	
-O(1)	2.546(7)	
-O(5)$^{(17)}$	2.659(7)	
-O(6)$^{(16)}$	2.871(7)	
Average	2.546	

Si(2)	r	O(5)$^{(17)}$-O(7)$^{(9)}$	2.59(2)	60.3(3)
Si(2)		O(6)$^{(16)}$-O(7)$^{(11)}$	2.66(2)	59.1(3)
M		O(7)$^{(9)}$-O(7)$^{(11)}$	2.73(2)	66.6(3)
		O(1)-O(5)$^{(17)}$	2.79(2)	64.8(3)
RE(3)	m	O(3)$^{(9)}$-O(9)	2.81(2)	69.3(3)
	r	O(2)$^{(11)}$-O(6)$^{(16)}$	2.91(2)	66.3(3)
RE(3)		O(2)$^{(11)}$-O(3)$^{(9)}$	2.98(2)	76.3(3)
RE(3)		O(2)$^{(11)}$-O(9)	3.01(2)	75.7(3)
		O(3)$^{(9)}$-O(5)$^{(17)}$	3.04(2)	73.3(3)
		O(1)-O(6)$^{(16)}$	3.22(2)	72.6(3)
	m	O(1)-O(9)	3.32(2)	82.1(3)
		O(1)-O(7)$^{(9)}$	3.33(2)	82.7(3)
		O(5)$^{(17)}$-O(9)	3.34(2)	80.4(3)
		O(2)$^{(11)}$-O(7)$^{(11)}$	3.42(2)	89.5(4)
	m	O(1)-O(7)$^{(11)}$	3.49(2)	88.4(4)
		O(3)$^{(9)}$-O(7)$^{(9)}$	3.65(2)	95.8(4)
		O(6)$^{(16)}$-O(9)	3.79(3)	89.2(4)
	m	O(3)$^{(9)}$-O(7)$^{(11)}$	4.51(4)	134.6(5)
		Average	3.20	79.3

RE(3)

RE(3)-O(6)$^{(2)}$	2.457(7)	
-O(8)	2.492(7)	
-O(3)$^{(9)}$	2.540(7)	
-O(2)$^{(11)}$	2.549(7)	
-O(8)$^{(2)}$	2.582(7)	
-O(9)	2.640(7)	
-O(5)	2.669(7)	
-O(1)$^{(11)}$	2.953(7)	
Average	2.610	

Si(2)		O(6)$^{(2)}$-O(8)$^{(2)}$	2.62(2)	62.6(3)
Si(1)		O(1)$^{(11)}$-O(2)$^{(11)}$	2.63(2)	56.6(3)
Si(2)		O(5)-O(8)	2.64(2)	61.4(3)
		O(1)$^{(11)}$-O(5)	2.77(2)	58.7(3)
RE(2)		O(3)$^{(9)}$-O(9)	2.81(2)	65.6(3)
RE(1)	r	O(5)-O(6)$^{(2)}$	2.92(2)	68.9(3)
		O(2)$^{(11)}$-O(8)	2.96(2)	71.9(3)
		O(8)$^{(2)}$-O(9)	2.96(2)	69.1(3)
RE(2)		O(2)$^{(11)}$-O(3)$^{(9)}$	2.98(2)	71.6(3)
	m	O(3)$^{(9)}$-O(8)$^{(2)}$	3.00(2)	71.8(3)
RE(2)	r	O(2)$^{(11)}$-O(9)	3.01(2)	71.0(3)
	m	O(1)$^{(11)}$-O(8)	3.42(2)	77.2(4)
		O(8)-O(9)	3.59(2)	88.7(4)
		O(3)$^{(9)}$-O(6)$^{(2)}$	3.65(2)	93.7(4)
		O(1)$^{(11)}$-O(6)$^{(2)}$	4.03(3)	95.9(4)
	m	O(1)$^{(11)}$-O(3)$^{(9)}$	4.05(3)	94.6(4)
		O(5)-O(8)$^{(2)}$	4.57(3)	120.5(5)
	m	O(8)-O(8)$^{(2)}$	4.57(3)	128.3(5)
		Average	3.29	79.3

M

3 M-O(7)$^{(3)}$	2.049(10)	
3 -O(4)	2.096(10)	
Average	2.072	

RE(2)	3 O(7)$^{(3)}$-O(7)$^{(4)}$	2.73(2)	83.4(6)
RE(1)	3 O(4)-O(4)$^{(1)}$	2.89(2)	87.0(6)
	3 O(4)-O(7)$^{(3)}$	3.02(2)	93.5(6)
	3 O(4)-O(7)$^{(5)}$	3.08(2)	96.1(6)
	Average	2.93	90.0°

Si(1)

Si(1)-O(4)$^{(7)}$	1.609(8)	
-O(3)	1.616(8)	
-O(2)	1.638(8)	
-O(1)	1.662(8)	
Average	1.631	

RE(1)	O(2)-O(4)$^{(7)}$	2.55(2)	103.6(5)
RE(1)	O(3)-O(4)$^{(7)}$	2.58(2)	105.7(5)
RE(3)	O(1)-O(2)	2.63(2)	105.8(5)
	O(1)-O(4)$^{(7)}$	2.69(2)	110.7(5)
	O(2)-O(3)	2.76(2)	115.7(5)
	O(1)-O(3)	2.76(2)	114.7(5)
	Average	2.66	109.4

†Estimated standard errors in parentheses refer to the last digit. The equivalent positions (referred to Table 1) are designated as superscripts and are (1) = -y, x-y, z; (2) = y-x, -x, z; (3) = -y, -x, ½+z; (4) = x, x-y, ½+z; (5) = y-x, y, ½+z; (6) = 2/3+x, 1/3+y, 1/3+z; (7) 2/3-y, 1/3+x-y, 1/3+z; (8) = 2/3+y-x, 1/3 -x, 1/3+z; (9) = 2/3 -y, 1/3 -x, 5/6+z; (10) = 2/3+x, 1/3 +x-y, 5/6 +z; (11) = 2/3 +y-x, 1/3 +y, 5/6 +z; (12) = 1/3+x, 2/3 +y, 2/3 +z; (13) = 1/3 -y, 2/3 +x-y, 2/3 +z; (14) = 1/3 +y-x, 2/3 -x, 2/3 +z; (15) = 1/3 -y, 2/3 -x, 1/6 +z; (16) = 1/3+x, 2/3 +x-y, 1/6 +z; (17) = 1/3 +y-x, 2/3 +y, 1/6 +z.

Cations which share polyhedral edges are noted on the left. Ridgepole (= r) and meridional edges are also noted. Note that RE–OH(1,2,3) distances are listed under OH(1,2,3) and are not included in the RE–O bond distance averages.

Table 3. (continued)

	Si(2)				OH(1)				OH(2)	
	Si(2)-O(8)[9]	1.620(8)		1	OH(1)-OH(1a)	1.00(14)		1	OH(2)-Ca(x)	2.46(5)
	-O(5)[9]	1.623(8)		3	-RE(1)	2.52(1)		3	-RE(2)	2.61(1)
	-O(7)[4]	1.628(8)		3	-O(4)	2.72(2)		3	-O(7)	2.66(2)
	-O(6)[9]	1.636(8)		1	-OH(3)	2.79(2)				
	Average	1.627			OH(1a)				OH(3)	
RE(2)	O(5)[9]-O(7)[4]	2.59(2)	105.7(5)	1	OH(1a)-OH(1)	1.00(14)		3	OH(3)-RE(3)	2.47(4)
RE(3)	O(6)[9]-O(8)[9]	2.62(2)	107.2(5)	3	-O(4)	2.03(5)		3	-O(8)	2.70(5)
RE(3)	O(5)[9]-O(8)[9]	2.64(2)	107.6(6)	3	-RE(1)	2.39(4)		1	-OH(1)	2.79(4)
RE(2)	O(6)[9]-O(7)[4]	2.66(2)	109.0(5)	1	-M	2.43(5)				
	O(7)[4]-O(8)[9]	2.69(2)	111.6(5)						Ca(x)	
	O(5)[9]-O(6)[9]	2.76(2)	115.8(6)		OH					
	Average	2.66	109.5	1	OH-Si(c)	1.69(2)		1	Ca(x)-OH	1.82(5)
				1	-Ca(x)	1.82(5)		1	-OH(2)	2.46(5)
	Si(c)			3	-O(9)	2.67(2)		3	-O(1)	2.64(4)
	3 Si(c)-O(9)	1.631(8)		3	-O(1)	2.71(3)		3	-O(3)	3.04(5)
	1 -OH	1.686(7)								
	Average	1.645								
	3 O(9)-OH	2.67(2)	107.1(5)							
	3 O(9)-O(9)[1]	2.70(2)	111.7(5)							
	Average	2.68	109.4							
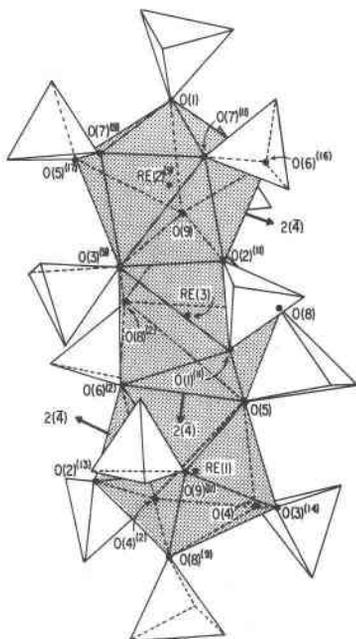
Fig. 1. Cerite: unit of rod II showing REO_8 $D2d$ dodecahedra, loci of pseudo 2-fold ($\bar{4}$) axes and circumjacent SiO_4 tetrahedra. Atoms are labelled according to Table 3. The drawing is a Penfield projection.

agreement for large cation contents and supports the subtraction of bastnäsite as an impurity phase. The role of H_2O remains a problem.

Mg^{2+} is the predominant octahedrally coordinated cation which could reside in M, but Al^{3+} and Fe^{3+} are also present in substantial amounts. This site is believed to be

Table 4. Cerite: cell contents along rod I at 00z, etc.[†]

	Whitlockite					Cerite		
Atom	z	K			Atom	z	K	
M	0.000	6.00			M	0.000	8.76	
□(1)	.10	--			OH(1a)	.064	0.58	
O(1A')	.193	1.14			OH(1)	.090	6.00	
P(A')	.234	1.14			OH(3)	.163	5.62	
P(A)	.255	4.86			Si(c)	.252	5.17	
O(1A)	.298	4.86			OH	.297	5.20	
Ca(IIA')	.312	0.57			Ca(x)	.344	1.01	
□(2)	.40	--			OH(2)	.409	6.00	
	x	y	z			x	y	z
O(IIA')	0.138	0.000	0.250	3.43				
O(IIA)	.150	.019	.242	14.57	O(9)	.160	.039	.240	18.00

[†]The atom labels in Calvo and Gopal (1975) for whitlockite and cerite in this study are retained. The variable parameter, $\underline{z}$, in 00$\underline{z}$ is listed. The cell contents are listed under K. Note that K for M was based on the scattering curve for Mg^{2+}.

Table 5. Cerite: chemical analysis and interpretation

	1	2	3	4		5	6	7
Ce_2O_3	35.73	29.08	35.05	3.90		9	73.36	35.61
La_2O_3 etc.	31.53	24.93	30.04	3.37		-	-	30.08
CaO	3.72	3.72	4.48	1.46	}8.98	-	-	4.49
BaO	0.37	0.37	0.45	0.05		-	-	0.42
Na_2O	0.20	0.20	0.24	0.14		-	-	0.24
K_2O	0.13	0.13	0.16	0.06		-	-	0.16
MgO	1.58	1.58	1.90	0.86		-	-	1.35
MnO	0.17	0.17	0.20	0.05		-	-	-
Al_2O_3	0.95	0.95	1.14	0.41	}1.55	-	-	-
Fe_2O_3	0.76	0.76	0.92	0.21		1	3.96	1.71
TiO_2	0.07	0.07	0.08	0.02		-	-	-
CO_2	3.56	-	-	-		-	-	-
SiO_2	18.46	18.46	22.24	6.76	}6.79	7	20.89	22.49
SO_3	0.12	0.12	0.14	0.03		-	-	0.13
F	1.60	0.06	0.07	-		-	-	-
$H_2O(-)$	0.14	0.14	0.17	-		-	-	-
$H_2O(+)$	2.26	2.26	2.72	5.53		2	1.79	3.32
O = 2F	-0.67	-	-	-		-	-	-
Total	100.68	83.00	100.00				100.00	100.00

[1]Glass et al. (1958) on Mountain Pass material.

[2](1) less 17.7% bästnasite, $CeLaF_2(CO_3)_2$, assuming total contributions to CO_2. The Ce:La = 1:1 ratio was arbitrarily selected.

[3]Column 2 renormalized to 100.00%.

[4]Calculated cations in formula unit, Z = 6. This derived from column 3, the specific gravity of 4.78 in Glass et al. and the cell parameters reported in this study.

[5]Ideal atomic contents, for $RE_8^{3+}Fe^{3+}(SiO_4)_6(SiO_3OH)(OH)_3$.

[6]Computed formula based on column 5, with $RE^{3+} = Ce^{3+}$.

[7]Computed formula based on (A) in the text.

fully occupied; although we employed a scattering curve for Mg^{2+}, the site population refinement gave 1.46 Mg atoms per site (Table 1), suggesting the presence of a heavier cationic species. We propose that the first series transition metal cations, most notably Fe^{3+}, partition at this site. The site population refinement suggests ca. 0.39 Fe^{3+} at this site. This would yield an average $^{[6]}(Mg_{0.61}^{2+}Fe_{0.39}^{3+})-O = 2.09Å$ distance, close to 2.07Å in Table 3 for this site.

The distribution of atoms along rod I at $00z$ is summarized in Table 4. Splitting of Si(c) into two parts such that their total equals 1 is evident in whitlockite. For cerite, we could not find evidence for a corresponding splitting, because but little residual electron density would remain (0.83/6 × 14 = 1.9 electrons) and because cerite includes major lanthanide ions. In the absence of further evidence, we prefer to accept the theoretical formula for cerite in much the same sense as the complementary relationship between P(A) and P(A') in whitlockite. The OH(1a)–OH(1) distance of 1.00Å suggests a cooperative relationship. Although our refinement assumed site population of 1.00 for OH(1), OH(1a) refined to site population 0.10. We suspect that OH(1) is probably reduced to site population 0.90. OH(3) has site population 0.94. This site may indeed be fully occupied. Ca(x) closely matches the position for Ca(IIA') in whitlockite. It is only weakly populated in cerite, as it is in whitlockite. The Ca(x)–OH = 1.82Å distance is short and therefore a cooperative

[Ca(x),OH] relationship is suggested. Indeed, adding their site populations we get 0.17 + 0.87 = 1.04. This sum could easily be reduced to 1.00 if some RE cations substitute for Ca(x). In fact if Ca(x) = Ce^{3+}, the site population would be approximately 0.06. OH(2), which was assumed fully occupied, roughly matches the vacant position, □(2), in whitlockite, just as OH(1) approximates □(1). OH(3) approximates the P(A')–O(1A') positions in whitlockite which are evidently absent in cerite.

A neat interpretation can be effected which exploits some geometrical properties of the D2d dodecahedron of order 8 discussed in this paper. We recall that all three non-equivalent RE positions reside within the same kind of polyhedron, illustrated in Figure 2. Although this polyhedron can be constructed with 12 equilateral triangles, four pairs of such triangles are nearly coplanar and define rhombi, where two triangles share an edge defining the short diagonal of the rhombus. Therefore, the polyhedron can be considered as constructed from 8 vertices; 4 equilateral triangles and 4 rhombi; and 14 edges.

The anions situated on rod I along $00z$ bear a one-to-one correspondence with each of the three non-equivalent RE cations and bond to them. For example, RE(1)–OH(1) = 2.52, RE(2)–OH(2) = 2.61 and RE(3)–OH(3) = 2.47Å. Since these OH sites are largely occupied and since three RE atoms bond to each OH(1,2,3) on the 3-fold rotor, the OH(1,2,3) groups are electrostatically neutral. Furthermore, it is logical to propose that F^- cerites should exist. With the addition of the OH(1,2,3) ligands, the coordination number increases to 9 for each non-equivalent RE cation. The greater bond strength of RE^{3+}–O compared with Ca^{2+}–O appears to be the deciding factor in the incorporation of additional $(OH)^-$ ions into the coordination sphere relative to the Ca–O polyhedron in whitlockite. This phenomenon may explain the great diversity of exotic RE silicates compared with the Ca phosphates.

The mode of the additional bond is very interesting: in
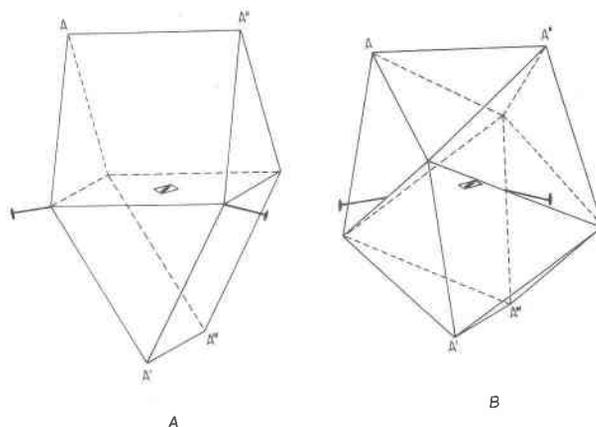
Fig. 2. Penfield projections of (a) the D2d gable disphenoid and (b) the D2d dodecahedron. Both polyhedra are of order 8.

Table 6. Cerite: electrostatic valence balance of cations and anions†

Anions	[9]RE(1)³⁺	[9]RE(2)³⁺	[9]RE(3)³⁺	[6]M³⁺	[4]Si(1)⁴⁺	[4]Si(2)⁴⁺	[4]Si(c)⁴⁺	Δp₀
O(1)	-----	+0.000	+0.343	-----	+0.031	-----	-----	-0.33
O(2)	+0.034	-0.149	-0.061	-----	+0.007	-----	-----	+0.00
O(3)	+0.229	-0.125	-0.070	-----	-0.015	-----	-----	+0.00
O(4)	-0.101 -0.090	-----	-----	+0.024	-0.022	-----	-----	-0.17
O(5)	-0.184	+0.113	+0.059	-----	-----	-0.004	-----	+0.00
O(6)	-0.062	+0.325	-0.153	-----	-----	+0.009	-----	+0.00
O(7)	-----	-0.081 -0.050	-----	-0.023	-----	+0.001	-----	-0.17
O(8)	-0.140	-----	-0.118 -0.028	-----	-----	-0.007	-----	-0.33
O(9)	+0.311	-0.033	+0.030	-----	-----	-----	-0.014	+0.00
OH	-----	-----	-----	-----	-----	-----	+0.041	+0.00
OH(1)	3×(-0.07)	-----	-----	-----	-----	-----	-----	+0.00
OH(2)	-----	3×(+0.06)	-----	-----	-----	-----	-----	+0.00
OH(3)	-----	-----	3×(-0.14)	-----	-----	-----	-----	+0.00

†A bond length deviation refers to the polyhedral average subtracted from the individual bond distance. RE averages in Table 3 were taken. The Δp_0 = deviations of electrostatic bond strength sum from neutrality (p_0 = 2.00 e.s.u.). The ideal formula $RE_9^{3+}Fe^{3+}(SiO_4)_6(SiO_3OH)(OH)_3$ was selected.

each case, the bond is through one of the rhombi. The rhombi in question are $O(4)^{(2)}–O(4)–O(5)–O(6)^{(2)}$ for RE(1); $O(7)^{(11)}–O(7)^{(9)}–O(3)^{(9)}–O(2)^{(11)}$ for RE(2); and $O(8)^{(2)}–O(6)^{(2)}–O(8)–O(9)$ for RE(3). In each case, the short diagonal edge of the rhombus is opened up in cerite, viz. $O(4)^{(2)}–O(5) = 4.59$ for RE(1); $O(3)^{(9)}–O(7)^{(11)} = 4.51$ for RE(2); $O(8)–O(8)^{(2)} = 4.57$Å for RE(3). These are compared with edge distance averages of 3.2–3.4Å for the D2d dodecahedron in cerite (Table 3).

Summing up, accepting all sites, occupancies and chemical analysis, our crystal formula can be written for Z = 6:

$$(Ce_{3.90}^{3+}La_{etc.,}^{3+} {}_{3.37}Ca_{1.46}^{2+}Ba_{0.05}^{2+}Na_{0.14}^{1+}K_{0.06}^{1+})_{\Sigma=8.98}$$

$$(Si_{6.83}^{4+}S_{0.03}^{6+})_{\Sigma=6.86}(Mg_{0.61}Fe_{0.39}^{3+})_{\Sigma=1.00}$$

$$Ca_{0.17}^{2+}O_{25.68}(OH)_{0.86}(OH)_{3.03} \qquad (A)$$
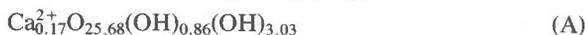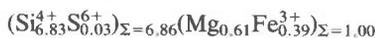
and suggests an ideal end-member formula $RE_9^{3+}Fe^{3+}(SiO_4)_6(SiO_3OH)(OH)_3$. The Fe^{3+} content required by this formula is admittedly higher than that reported in Table 5, columns 3 and 6, but presently we see no superior explanation of the high site multiplicity (1.46, based on Mg^{2+} scattering curve: cf. Table 1).

With three additional anions in the formula unit over total anions in whitlockite, cerite is an efficiently packed structure indeed, with $V_E = 20.59$Å³ per anions, rivalling the densest oxysalts which are derived from the glaserite structure type.

Electrostatic valence balances and bond distances

From the effective ionic radii of Shannon and Prewitt (1969), the average bond distances are anticipated to be $^{[8]}Ce^{3+}–^{[3.5]}O^{2-} = 2.51$Å, $^{[8]}La^{3+}–^{[3.5]}O^{2-} = 2.55$Å and $^{[8]}Ca^{2+}–^{[3.5]}O^{2-} = 2.49$Å. The mean $^{[8]}RE(1)–O = 2.60$, $^{[8]}RE(2)–O = 2.55$ and $^{[8]}RE(3)–O = 2.61$Å for the oxide fraction in Table 3 are all slightly larger than these values, but relatively few data comprised the Shannon and Prewitt tables, and none represent silicates. The differences, however, are very small. In addition, our cerite apparently contains a wide range of different ions in solution at these sites.

Bond length–bond strength electrostatic valence balances are tabulated in Table 6. Here some drastic assumptions were made. First, the ideal $RE_9^{3+}Fe^{3+}(SiO_4)_6(SiO_3OH)(OH)_3$ formula was invoked. Second, since H-positions could not be located, the $(OH)^-$ ions were treated as fluoride ions, for example. Some guesses can be made about the behavior of the protons from Table 3. The $OH(1)–OH(3) = 2.79$Å distance suggests a possible symmetrical bond. The $OH(1)–O(4) = 2.72$Å and $OH(3)–O(8) = 2.70$Å are also possible. Here, the protons would be tightly constrained on the 3-fold rotor by the oxoanions in general positions, or they may be disordered into three pieces. Likewise, $OH(2)–O(7) = 2.66$Å could behave the same way. Finally, the $OH–O(9) = 2.67$Å or $OH–O(1) = 2.71$Å bond could exist, the former unlikely because it is a SiO_3OH tetrahedral edge. The uncertainty in the role of the protons forces no conclusion on the OH^- ions in Table 6 since the O–H distances are not known.

With these assumptions in mind, nine anions are electrostatically neutral, four are electrostatically undersaturated. The polyhedral averages were those taken for the anhydrous RE-oxide bonds in Table 3. Since the system

is extensively neutral locally, negative deviations tend to be compensated by positive deviations in the same row. O(8), with $\Delta p_0 = -0.33$, has shorter bonds than the average. The only exception is O(1), with $\Delta p_0 = -0.33$. Here all bonds are longer than average. We suspect a disordered OH–O(1), possibly a disordered symmetrical O–H–O(1) bond may account for this contradiction.

Acknowledgments

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