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THE CRYSTAL STRUCTURE OF GERENITE-(Y), $(Ca,Na)_2(Y,REE)_3Si_6O_{18}\cdot 2H_2O$, A CYCLOSILICATE MINERAL

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ABSTRACT

The crystal structure of gerenite-(Y), ideally $(Ca,Na)_2(Y,REE)_3Si_6O_{18}\cdot 2H_2O$, *a* 9.257(4), *b* 9.684(4), *c* 5.520(1) Å, α 97.36(3), β 100.52(3), γ 116.57(3)°, *V* 422.6(3) Å^3, space group $P\bar{1}$, $Z = 1$, has been solved by direct methods, and refined to an *R* index of 5.2% based on 2175 unique reflections measured with Mo*K*α radiation. The structure consists of the following elements: (1) Si_6O_{18} rings, oriented approximately parallel to $(\bar{1}01)$, (2) chains of edge-sharing $Y(1)O_6$ and $Y(2)O_6$ octahedra oriented approximately parallel to [101], and (3) $Ca\phi_8$ polyhedra. The Si_6O_{18} rings share corners with the chains of YO_6 octahedra to form a three-dimensional framework. The Ca positions are located outside of and between pairs of Si_6O_{18} rings. Bond-valence analysis shows that one of the apical anions coordinating the cation at the Ca position is a molecule of H_2O. The $Ca\phi_8$ polyhedra share corners and edges with adjacent Si_6O_{18} rings and YO_6 chains. The crystal structure of gerenite-(Y) has elements similar to those of kainosite-(Y) and leifite, both of which occur with gerenite-(Y) at the Strange Lake locality.

Keywords: gerenite-(Y), crystal structure, cyclosilicate, Strange Lake, Quebec – Labrador.

SOMMAIRE

La structure cristalline de la gerenite-(Y) (prononciation: *guèrenite*), de formule idéale $(Ca,Na)_2(Y,TR)_3Si_6O_{18}\cdot 2H_2O$ (*TR*: terres rares), *a* 9.257(4), *b* 9.684(4), *c* 5.520(1) Å, α 97.36(3), β 100.52(3), γ 116.57(3)°, *V* 422.6(3) Å^3, groupe spatial $P\bar{1}$, $Z = 1$, a été établie par méthodes directes jusqu'à un index *R* de 5.2% en utilisant 2175 réflexions uniques mesurées avec rayonnement Mo*K*α. La structure contient les éléments structuraux suivants: (1) des anneaux Si_6O_{18} orientés plus ou moins parallèles à $(\bar{1}01)$, (2) des chaînes d'octaèdres $Y(1)O_6$ et $Y(2)O_5$ à arêtes partagées, à peu près parallèles à [101], et (3) des polyèdres $Ca\phi_8$. Les anneaux Si_6O_{18} partagent leur coins avec les chaînes d'octaèdres YO_6 pour ainsi former une trame tridimensionnelle. Les positions occupées par le Ca sont externes par rapport aux anneaux de Si_6O_{18} ou entre ceux-ci. Une analyse des valences de liaison montre qu'un des anions apicaux en coordinence avec le Ca est une molécule de H_2O. Les polyèdres $Ca\phi_8$ partagent des coins et des arêtes avec les anneaux Si_6O_{18} et les chaînes YO_6 adjacents. La structure de la gerenite-(Y) ressemble en certains points à celle de la kainosite-(Y) et de la leifite, que l'on retrouve avec la gerenite-(Y) au gisement de Strange Lake.

(Traduit par la Rédaction)

Mots-clés: gerenite-(Y), structure cristalline, cyclosilicate, Strange Lake, Québec – Labrador.

INTRODUCTION

As described in Jambor *et al.* (1998), gerenite-(Y) occurs in the Strange Lake peralkaline granitic complex, about 250 km northeast of Schefferville, on the Quebec – Labrador border. The intrusive complex contains a deposit of Y, the rare-earth elements (*REE*), Nb, Zr and Be, mostly within a thick lens of pegmatite and aplite. In addition to gerenite-(Y), the pegmatite – aplite lens contains quartz, albite, K-feldspar, aegirine, riebeckite – arfvedsonite, gittinsite, zircon and kainosite-(Y), and small amounts of pyrochlore, thorite, a new gadolinite-type mineral, titanite, fluorite, epidote, hematite, monazite-(Ce), and sphalerite (Miller 1996, Jambor *et al.* 1998).

Most gerenite-(Y) occurs in the pegmatite – aplite lens as anhedral masses composed of an intergrowth of gerenite-(Y), kainosite-(Y), and quartz. The gerenite-(Y) typically forms bundles (100 × 20 μm) of slightly divergent elongate grains with interstitial quartz. According to Miller (1996), the anhedral masses may be pseudomorphic after leifite. Gerenite-(Y) also occurs in the pegmatite – aplite lens as elongate, prismatic grains of primary origin.

Using precession photographs of a crystal from an intergrowth, Jambor *et al.* (1998) concluded that

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gerenite-(Y) is triclinic (space group $P1$ or $P\bar{1}$). The unit-cell parameters (refined from powder data) are a 9.245(5), b 9.684(6), c 5.510(3) Å, α 97.44(6), β 100.40(6), γ 116.70(6)°, V 420.8(1) Å^3. The average chemical composition (based on results of three electron-microprobe analyses by D.R. Owens) is (in wt.%) Na_2O 1.7, CaO 7.6, MnO 0.6, Y_2O_3 28.2, Ce_2O_3 0.1, Nd_2O_3 0.2, Sm_2O_3 0.3, Gd_2O_3 1.1, Tb_2O_3 (estimated from chondrite-normalized *REE* spectra) 0.34, Dy_2O_3 4.0, Ho_2O_3 (estimated) 1.05, Er_2O_3 3.6, Tm_2O_3 (estimated) 0.51, Yb_2O_3 2.9, Lu_2O_3 (estimated) 0.41, SiO_2 40.5, H_2O (by difference) 6.89, total 100.0. Recalculation on the basis of 18 O atoms gave (in atoms per formula unit) Na 0.49, Ca 1.21, Y 2.24, *REE* 0.69, Si 6.04 and H_2O 3.43. This study was undertaken to determine the crystal structure of gerenite-(Y) and to study the role of H_2O in the structure.

TABLE 1. MISCELLANEOUS INFORMATION: GERENITE-(Y)

a (Å)	9.257(4)	Z	1
b	9.684(4)	Crystal size (mm)	0.1 × 0.1 × 0.01
c	5.520(1)	μ (Mo$K\alpha$; mm^{-1})	12.10
α (°)	97.38(3)	Rad/mono	Mo$K\alpha$/graphite
β	100.52(3)	Total $\lvert F_o \rvert$	2175
γ	116.57(3)	$[I \geq 3\sigma \cdot (I)]$	1369
V (Å^3)	422.6(3)	R (%)	5.2
Space group	$P\bar{1}$	wR (%)	6.8

$R = \sum \lvert F_o - F_c \rvert / \sum F_o$

$wR = \left[\sum \left(w \cdot \lvert F_o - F_c \rvert \right)^2 / \sum w \cdot F_o^2 \right]^{0.5}$, $w = \left[\sigma^2 F + 0.004567 F^2 \right]^{-1}$

Experimental

The crystal used in this study was of the prismatic (primary) type, obtained (as a plate) from a thin section. The bounding face was a polished surface with approximate index (011). The crystal was mounted on a Siemens *P3* automated four-circle diffractometer equipped with a molybdenum-target X-ray tube (operating at 50 kV, 35 mA) and a precisely oriented graphite crystal monochromator mounted with equatorial geometry. Forty-two reflections with 15.06 < 2θ < 32.56° were centered using an automated search routine, and the correct unit-cell was selected from an array of real-space vectors corresponding to potential unit-cell axes. Least-squares refinement of these reflections produced the cell dimensions given in Table 1, together with the orientation matrix relating the crystal axes to the diffractometer axes. The cell dimensions are almost identical to those reported in Jambor *et al.* (1998). Intensity data were collected in the θ–2θ scan mode, using 96 steps with a scan range from [2θ (Mo$K\alpha_1$) – 1.1]° to [2θ (Mo$K\alpha_2$) + 1.1]° and a variable scan-rate between 0.5 and 29.3°/min depending on the intensity of an initial one-second count at the center of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. The stability of the crystal alignment was monitored by collecting two standard reflections every 23 measurements. A complete sphere of reflections (4944 measurements, exclusive of standards) was collected from 3 to 60° 2θ. Forty-seven of the reflections were rejected because of asymmetrical backgrounds. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°, after the method of North *et al.* (1968). These data (362 measurements) were used to calculate an absorption correction. The crystal was modeled as a thin plate with approximate index ($\bar{2}$ 11 11). A minimum glancing angle of 5° resulted in the loss of 38 reflections. The merging R index for the ψ-scan data set decreased from 6.9% before the absorption correction to 4.2% after the absorption correction. This correction was then applied to the entire dataset; minimum and maximum transmissions were 0.368 and 0.588, respectively. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 2175 unique reflections, 1369 were classed as observed [I ≥ 3σ(I)].

Structure Solution and Refinement

The Siemens SHELXTL PC system of programs was used throughout this study. Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The scattering curve for Ho was used to represent the rare-earth elements (*REE*) on the basis of the weighted average of the atomic numbers, calculated from the average results of the electron-microprobe analyses in Jambor *et al.* (1998). Miscellaneous information on data collection and refinement is given in Table 1.

A mean [E^2 – 1] value of 0.89 implies a centrosymmetric space-group. Systematic absences in the complete data-set suggested space group $P\bar{1}$. The structure was solved by direct methods and refined in $P\bar{1}$ to an R index of 9.9% for an isotropic displacement model. Further refinement was done using anisotropic displacement factors for all atoms in the structure. Assuming full occupancy for all sites (and refining Ca:Na and Y:*REE* for the Ca and Y sites, respectively) led to convergence at R and wR indices of 5.1 and 5.2%, respectively. However, the results show excess positive charge at the Ca position, as the Ca:Na ratio is 1:0.56, and the bond-valence sum to the Ca position is 1.87. These values must be 1:1 and 1.5, respectively, if the Y sites are fully occupied by trivalent cations, and the H_2O site is fully occupied by H_2O (as indicated by the bond-valence value of 0.33 valence units). The results suggest that there are vacancies at the Ca and

Y sites. Additional refinements were done with the occupancies fixed at the values given by the electron-microprobe results (including estimated elements). This resulted in final R and wR values of 5.2 and 6.8%, respectively (8.8 and 9.4% for all 2175 data). Addition of an isotropic extinction correction did not improve the results. The program MISSYM (Le Page 1987) was used to search for additional elements of symmetry; none was indicated. Positional coordinates and anisotropic and equivalent isotropic-displacement factors are given in Table 2. Interatomic distances and angles are given in Table 3, and a bond-valence analysis in Table 4. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

Description of the Structure

There are six distinct cation sites in the gerenite-(Y) structure. Three of the cation sites are occupied by Si. The Si(1)–O distances range from 1.580 to 1.623 Å (mean 1.606 Å), and the O–Si(1)–O angles, from 104.2 to 116.1° (mean 109.4°). The Si(2)–O distances vary from 1.600 to 1.632 Å (mean 1.616 Å), and the O–Si(2)–O angles, from 105.4 to 117.1° (mean 109.3°). The Si(3)–O distances range from 1.591 to 1.644 Å (mean 1.616 Å), and the O–Si(3)–O angles, from 104.8 to 115.7° (mean 109.4°). The Si(1) tetrahedron is somewhat smaller than the Si(2) and Si(3) tetrahedra; the polyhedral volumes are 2.11 and 2.15 (× 2) Å^3, respectively.

The SiO_4 tetrahedra share corners to form $[Si_6O_{18}]^{12-}$ rings oriented approximately parallel to $(\bar{1}01)$ (Figs. 1, 2). The bridging O atoms are O(4), O(8) and O(9). In general, the bonds to the bridging O atoms are longer than those to the non-bridging O atoms (Table 2). The Si(1)–Si(2) and Si(1)–Si(3) distances are similar (3.211 and 3.225 Å), as are the Si(1)–O(9)–Si(2) and Si(1)–O(8)–Si(3) angles (167.1 and 167.3°). The Si(2)–Si(3) distance is somewhat shorter (3.108 Å), and the Si(2)–O(4)–Si(3) angle is more acute (145.8°). The lengths of the edges of the Si_6O_{18} ring are approximately identical (2.58, 2.59, and 2.59 Å, all ×2). However, the distance across the ring between the symmetry-related O(9) atoms is much shorter (4.86 Å) than the distance between O(4) and O(8) pairs (5.23 and 5.27 Å, respectively).

The atom at the Y(1) site, at special position 1e (½, ½, 0), is coordinated by six O atoms, forming a distorted octahedron. The Y(1)–O distances are 2.207, 2.300, and 2.315 Å (all ×2; mean 2.274 Å), and the O–Y(1)–O angles range from 72.8 to 107.2° (mean 90.0°). The mean quadratic elongation of the octahedra (Robinson *et al.* 1971) is 1.033, and the polyhedron's volume is 14.95 Å^3.

The atom at the Y(2) site is coordinated by six O atoms, forming a distorted octahedron. The Y(2)–O distances range from 2.220 to 2.326 Å (mean 2.279 Å), and the O–Y(2)–O angles range from 73.7 to 106.5° (mean 90.5°). The mean quadratic elongation of the octahedron is 1.033, and the polyhedron's volume is 15.03 Å^3.

The Y(1) and Y(2) octahedra share edges to form chains with the repeat pattern Y(1), Y(2), Y(2)... The chains of octahedra run approximately parallel to [101]. Each Y(1) octahedron shares two O(3)–O(5) edges with two Y(2) octahedra. The two shared edges are considerably shorter (2.74 Å) than the ten unshared

TABLE 2. ATOMIC PARAMETERS FOR GERENITE-(Y)

Atom	x	y	z	U_{11}*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Si(1)	0.3647(3)	0.2508(3)	0.3825(5)	139(12)	138(14)	77(12)	84(11)	34(9)	32(10)	110(10)
Si(2)	0.1195(3)	0.3680(3)	0.1021(5)	111(11)	132(14)	71(12)	64(10)	31(9)	2(10)	104(10)
Si(3)	0.7595(3)	0.1251(4)	0.7688(5)	134(12)	174(14)	70(12)	97(11)	34(9)	16(10)	117(11)
Y(1)	1/2	1/2	0	314(7)	238(7)	109(6)	217(6)	-93(5)	-63(5)	220(6)
Y(2)	0.7814(1)	0.3642(1)	0.3171(2)	103(3)	180(5)	78(4)	75(3)	21(2)	18(3)	119(3)
Ca	0.6211(4)	0.9329(4)	0.1730(6)	167(13)	178(14)	195(15)	95(12)	44(11)	46(11)	176(11)
O(1)	0.6699(9)	0.1554(10)	0.9775(16)	161(33)	180(39)	181(39)	83(31)	41(28)	-12(30)	180(30)
O(2)	0.5981(12)	0.7088(12)	0.3189(16)	402(48)	299(50)	40(35)	164(42)	-5(33)	9(31)	262(38)
O(3)	0.5221(11)	0.3437(11)	0.2696(20)	242(39)	265(50)	446(59)	165(39)	231(40)	215(45)	267(40)
O(4)	0.9611(9)	0.2183(11)	0.8895(16)	139(32)	260(45)	139(38)	58(33)	-29(27)	-88(31)	219(32)
O(5)	0.7600(11)	0.5145(11)	0.0394(18)	313(42)	250(47)	202(43)	132(38)	169(35)	99(35)	237(36)
O(6)	0.7081(9)	0.1625(10)	0.5040(15)	172(33)	187(39)	82(34)	44(30)	-24(26)	23(27)	173(29)
O(7)	0.0536(9)	0.4444(10)	0.3062(15)	137(30)	233(42)	126(36)	108(30)	63(26)	20(30)	156(30)
O(8)	0.2937(10)	0.0644(10)	0.2760(16)	227(36)	121(36)	192(40)	72(30)	3(30)	-44(29)	201(30)
O(9)	0.2238(14)	0.2935(14)	0.2480(22)	510(61)	482(68)	362(60)	449(59)	-137(46)	-57(49)	422(53)
OW	0.9081(16)	0.9984(20)	0.2675(27)	415(63)	872(119)	451(82)	318(75)	103(57)	169(78)	577(74)

*U_{ij} and U values are listed × 10^4

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR GERENITE-(Y)

Si(1)–O(2)a	1.580(9)		O(1)–Si(3)–O(4)		109.6(4)
–O(3)	1.619(11)		O(1)–Si(3)–O(6)		115.7(6)
–O(8)	1.601(9)		O(1)–Si(3)–O(8)d		105.0(5)
–O(9)	1.623(15)		O(4)–Si(3)–O(6)		111.5(5)
<Si(1)–O>	1.606		O(4)–Si(3)–O(8)d		104.8(6)
			O(6)–Si(3)–O(8)d		109.5(5)
Si(2)–O(4)b	1.632(7)		<O–Si(3)–O>		109.4
–O(5)c	1.600(10)				
–O(7)	1.622(10)		O(2)–Y(1)–O(3)	× 2	92.1(4)
–O(9)	1.609(16)		O(2)–Y(1)–O(3)c	× 2	87.9(4)
<Si(2)–O>	1.616		O(2)–Y(1)–O(5)	× 2	93.1(4)
			O(2)–Y(1)–O(5)c	× 2	86.9(4)
Si(3)–O(1)	1.607(10)		O(3)–Y(1)–O(5)	× 2	72.8(4)
–O(4)	1.621(8)		O(3)–Y(1)–O(5)c	× 2	107.2(4)
–O(6)	1.591(9)		<O–Y(1)–O>		90.0
–O(8)d	1.644(10)				
<Si(3)–O>	1.616		O(1)e–Y(2)–O(3)		88.6(3)
			O(1)e–Y(2)–O(5)		87.5(3)
Y(1)–O(2)	2.207(9)	× 2	O(1)e–Y(2)–O(6)		79.0(3)
–O(3)	2.300(12)	× 2	O(1)e–Y(2)–O(7)f		94.4(3)
–O(5)	2.315(11)	× 2	O(3)–Y(2)–O(5)		73.7(4)
<Y(1)–O>	2.274		O(3)–Y(2)–O(6)		90.3(4)
			O(3)–Y(2)–O(7)a		104.8(3)
Y(2)–O(1)e	2.263(8)		O(5)–Y(2)–O(7)a		102.4(3)
–O(3)	2.281(11)		O(5)–Y(2)–O(7)f		89.8(4)
–O(5)	2.286(11)		O(6)–Y(2)–O(7)a		94.1(3)
–O(6)	2.220(9)		O(6)–Y(2)–O(7)f		166.5(4)
–O(7)a	2.326(7)		O(7)a–Y(2)–O(7)f		74.7(4)
–O(7)f	2.296(8)		<O–Y(2)–O>		90.5
<Y(2)–O>	2.279				
			O(1)a–Ca–O(1)g		87.5(3)
Ca–O(1)a	2.370(9)		O(1)a–Ca–O(3)c		71.8(3)
–O(1)g	2.432(11)		O(1)a–Ca–O(6)h		101.6(3)
–O(2)	2.346(12)		O(1)a–Ca–O(8)a		109.7(3)
–O(3)c	2.977(10)		O(1)a–Ca–O(8)c		100.0(3)
–O(6)h	2.398(9)		O(1)g–Ca–O(3)c		103.3(3)
–O(8)a	2.994(10)		O(1)g–Ca–O(6)h		72.4(3)
–O(8)c	2.734(10)		O(1)g–Ca–O(8)a		128.8(3)
–OW	2.374(15)		O(1)g–Ca–O(8)c		59.6(3)
<Ca–O>	2.578		O(1)g–Ca–OW		92.6(5)
			O(2)–Ca–O(1)a		97.4(4)
O(2)a–Si(1)–O(3)	116.1(5)		O(2)–Ca–O(3)c		70.9(3)
O(2)a–Si(1)–O(8)	110.0(6)		O(2)–Ca–O(6)h		114.1(3)
O(2)a–Si(1)–O(9)	111.9(7)		O(2)–Ca–O(8)a		56.9(3)
O(3)–Si(1)–O(8)	107.2(6)		O(2)–Ca–O(8)c		111.5(4)
O(3)–Si(1)–O(9)	104.2(6)		O(2)–Ca–OW		81.4(5)
O(8)–Si(1)–O(9)	106.9(5)		O(3)c–Ca–O(8)a		127.7(3)
<O–Si(1)–O>	109.4		O(3)c–Ca–O(8)c		53.8(3)
			O(3)c–Ca–OW		100.1(5)
O(4)b–Si(2)–O(5)c	108.9(5)		O(6)h–Ca–O(8)a		57.3(3)
O(4)b–Si(2)–O(7)	110.3(5)		O(6)h–Ca–O(8)c		125.7(3)
O(4)b–Si(2)–O(9)	105.4(6)		O(6)h–Ca–OW		86.2(5)
O(5)c–Si(2)–O(7)	117.1(5)		O(8)a–Ca–OW		76.6(4)
O(5)c–Si(2)–O(9)	106.2(6)		O(8)c–Ca–OW		73.1(4)
O(7)–Si(2)–O(9)	108.1(6)		<O–Ca–O>		90.0
<O–Si(2)–O>	109.3				

Note: <M–ϕ> denotes the mean metal-ligand distance (Å). Equivalent positions: a = $\bar{x}$ + 1, $\bar{y}$ + 1, $\bar{z}$ + 1; b = x – 1, y, z – 1; c = $\bar{x}$ + 1, $\bar{y}$ + 1, $\bar{z}$; d = $\bar{x}$ + 1, $\bar{y}$, $\bar{z}$ + 1; e = x, y, z – 1; f = x + 1, y, z; g = x, y + 1, z – 1; h = x, y + 1, z.

edges (range 3.11 to 3.71 Å, mean 3.30 Å). Each Y(2) octahedron shares one O(3)–O(5) edge with a Y(1) octahedron and one O(7)–O(7) edge with another Y(2) octahedron. The shared edges are similar in length (2.74 and 2.80 Å), but much shorter than most of the unshared edges (range 2.85 to 3.65 Å, mean 3.31 Å). The chains share corners with the Si_6O_{18} rings to form a three-dimensional framework.

TABLE 4. BOND-VALENCE ARRANGEMENT IN GERENITE-(Y)

	Si(1)	Si(2)	Si(3)	Y(1)	Y(2)	Ca	Total
O(1)			1.05		0.50	0.27	2.05
						0.23	
O(2)	1.13			0.59 × 2 ↓		0.29	2.01
O(3)	1.01			0.46 × 2 ↓	0.48	0.05	2.00
O(4)		0.98	1.01				1.99
O(5)		1.07		0.44 × 2 ↓	0.48		1.99
O(6)			1.10		0.56	0.25	1.91
O(7)		1.01			0.42		1.89
					0.46		
O(8)	1.06		0.95			0.05	2.16
						0.10	
O(9)	1.00	1.04					2.04
OW						0.26	0.26
Total	4.20	4.10	4.11	2.98	2.90	1.50	

Bond valences (expressed in valence units) were calculated from the curves of Brese & O'Keeffe (1991), using the same site occupancies (Na and Ca in the Ca site, Y and *REE* in the Y sites) used in the structure refinement.

The atom at the Ca position is coordinated by eight anions, forming a distorted hexagonal dipyramid (Fig. 3). Bond-valence analysis (Table 4) shows that one of the apical anions (OW) is a molecule of H_2O, which contributes 0.26 valence units to the atom at the Ca position. The Ca–O,H_2O distances range from 2.346 to 2.994 (mean 2.578 Å); those to the apical O(1) and OW atoms are 2.370 and 2.374 Å, respectively. The O–Ca–O,H_2O angles vary from 53.8 to 128.8° (mean 90.0°). The polyhedron's volume is 26.95 Å^3.

The Ca positions are located just beyond and between pairs of Si_6O_{18} rings. The Caϕ$_8$ (ϕ: unspecified anion) dipyramid shares opposite equatorial O(1)–O(6) (2.85 Å) and O(2)–O(3) (3.13 Å) edges with Y(2) and Y(1) octahedra, respectively, from different chains. Adjacent equatorial O(1)–O(8) (2.58 Å) and O(3)–O(8) (2.59 Å) edges are shared with Si(1) and Si(3) tetrahedra, respectively, from one Si_6O_{18} ring. The opposite O(2)–O(8) (2.61 Å) and O(6)–O(8) (2.64 Å) edges are shared with Si(1) and Si(3) tetrahedra, respectively, from another Si_6O_{18} ring located above or below (±Z) the first. The dipyramid shares one non-equatorial O(1)–O(3) (3.18 Å) edge with the Y(2) octahedron adjacent to the Y(1) octahedron mentioned previously, and three other non-equatorial edges with other Ca polyhedra. The apical O(1) atom is also shared with an Si(3) atom in a third Si_6O_{18} ring (located in the ±X direction), in addition to the Y(2) octahedron, and another Ca atom. The apical OW atom is located above or below the center of the closest Si_6O_{18} ring, at a distance of ±1.82 and 0.48 Å from the planes formed by the Si and non-bridging O positions, respectively. There are two OW positions associated with each Si_6O_{18} ring. As noted previously, bond-valence analysis shows that the "atom" at the OW position is a molecule of H_2O. The most likely acceptor for hydrogen bonding is another molecule of H_2O at an adjacent OW position associated with a different Si_6O_{18} ring; the OW–OW distance is 2.80 Å. Other possibilities include oxygen

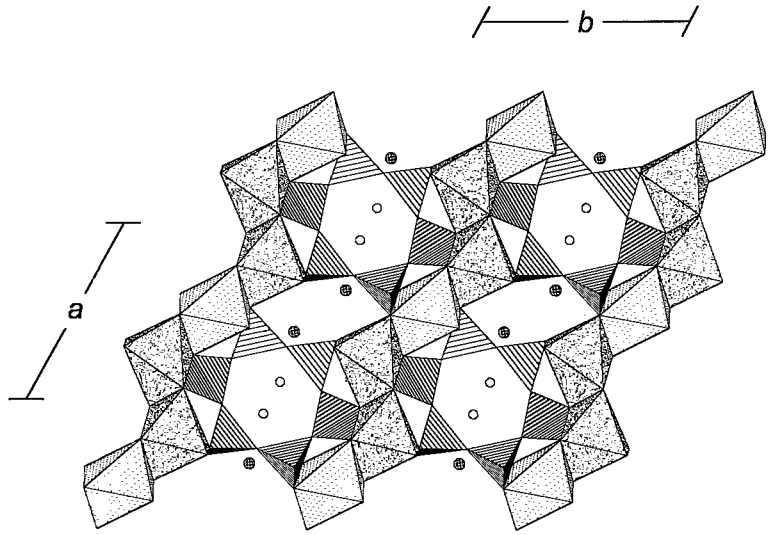

FIG. 1. The structure of gerenite-(Y) projected onto (001). The SiO_4 tetrahedra are ruled, the $Y(1)O_6$ octahedra are indicated by a regular dot pattern, and the $Y(2)O_6$ octahedra, by a random-dot pattern. The Ca atoms are shown as circles with crosses, and the H_2O molecules, as open circles.

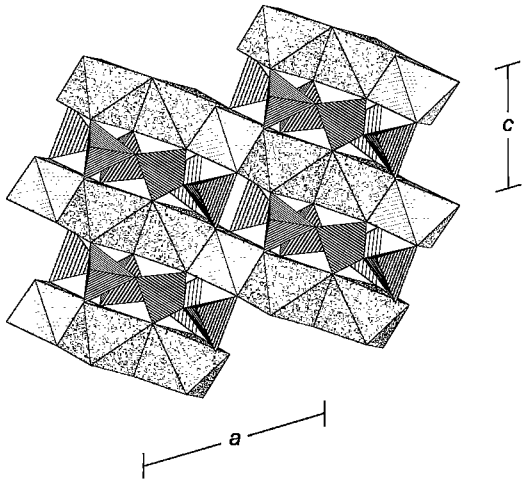

FIG. 2. The structure of gerenite-(Y) projected onto (010). The shading is the same as in the previous figure.

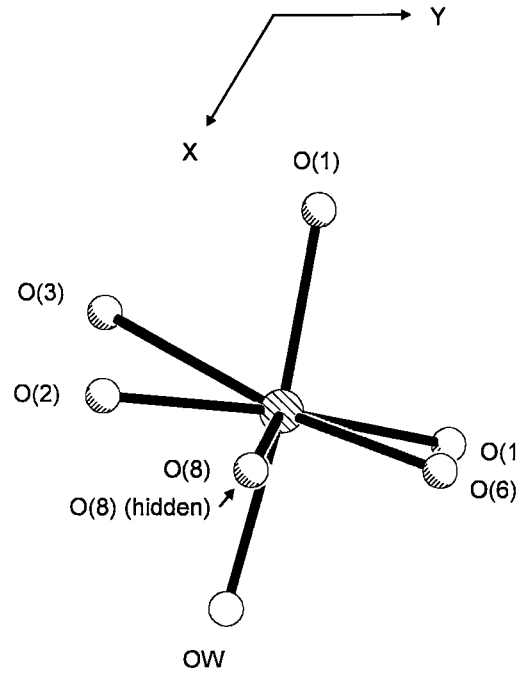

FIG. 3. Coordination of the Ca position in gerenite-(Y).

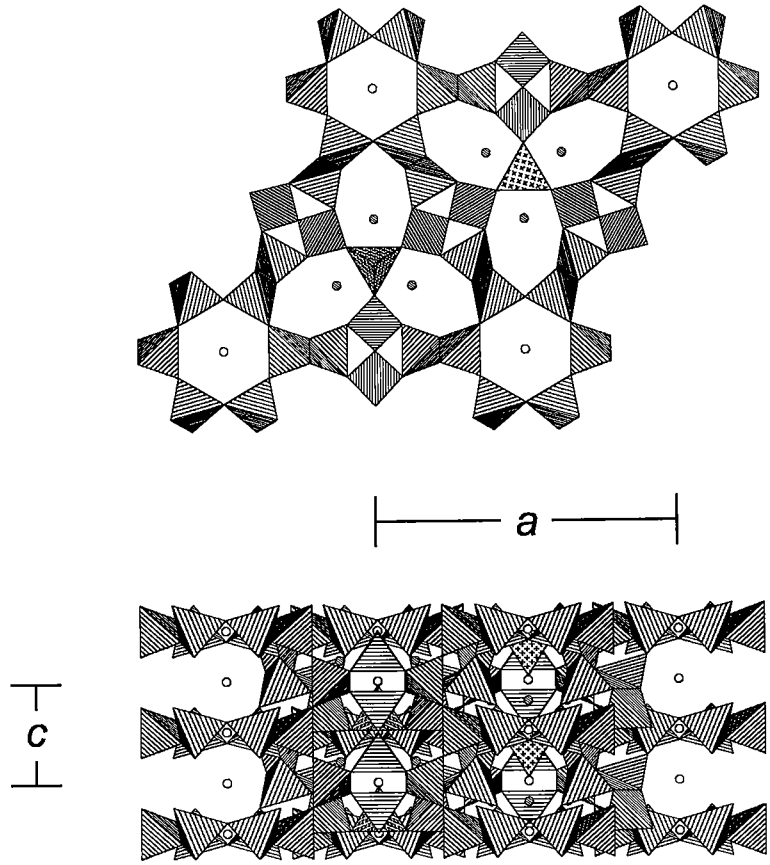

FIG. 4. The structure of kainosite-(Y) projected onto (001) (top) and (100) (bottom), as adapted from Giuseppetti *et al.* (1989). The SiO_4 tetrahedra are ruled, and the (Y,*REE*)O_8 polyhedra are indicated by a regular-dot pattern. The Ca atoms are shown as solid circles, the C atoms, as ruled circles, and the H_2O molecules, as open circles.

atoms at O(4) (2.97 Å) and O(9) (3.07 Å) positions. The Ca–OW–O(4) and Ca–OW–O(9) angles are 125.6° and 132.0°, respectively. However, the O(4)–OW–O(9) angle is only 92.5°, and the bond-valence sums to the O(4) and O(9) positions (Table 4) indicate that they are not involved in hydrogen bonding. A final possibility is another O(4) oxygen atom at a distance of 3.12 Å. However, it is unlikely that this is an acceptor, given the distance, the Ca–OW–O(4) angle of 89.1°, and the bond-valence sum to the O(4) position. Thus, the most likely acceptor for hydrogen bonding is the molecule of H_2O at an adjacent OW position.

DISCUSSION

The ideal formula of gerenite-(Y) is $(Ca,Na)_2(Y,REE)_3Si_6O_{18}•2H_2O$. The empirical formula of gerenite, based on the electron-microprobe data in Jambor *et al.* (1998), and calculated on the basis of six Si atoms (H_2O by stoichiometry), is $(Ca_{1.21}Na_{0.49}Mn_{0.08})_{\Sigma 1.78}(Y_{2.22}Dy_{0.19}Er_{0.17}Yb_{0.13}Gd_{0.05}Ho_{0.05}Sm_{0.02}Tb_{0.02}Tm_{0.02}Lu_{0.02}Ce_{0.01}Nd_{0.01})_{\Sigma 2.91}Si_6O_{19.89}H_{4.00}$. The formula based on the structure analysis is $(Ca_{1.21}Na_{0.57})_{\Sigma 1.78}(Y_{2.24}REE_{0.68})_{\Sigma 2.92}Si_6O_{18}•2H_2O$. It is interesting to note that selected results of electron-microprobe analyses of non-intergrowth gerenite-(Y) crystals show a Ca:Na ratio approximately 1:1 (Jambor *et al.* 1998); this may indicate fully occupied Ca and Y sites in these particular grains.

The results of the crystal-structure analysis show two H_2O molecules per formula unit, corresponding to approximately 4.1 wt.% H_2O. This is similar to the 3.9 wt.% obtained by Jambor *et al.* (1998) using the Penfield method, but much less than the 6.0 wt.%

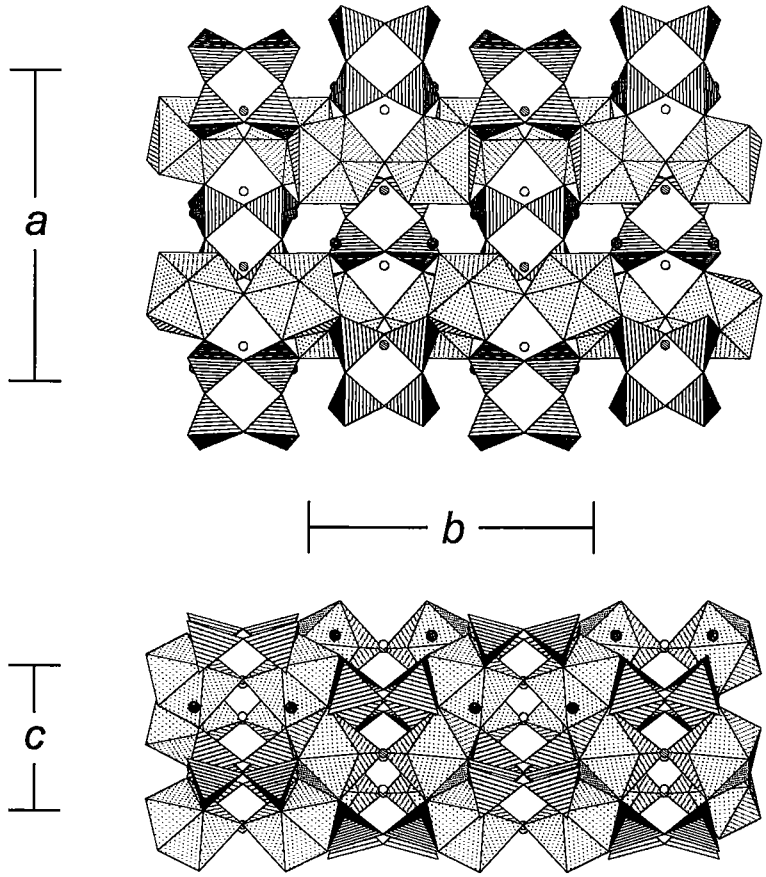

FIG. 5. The structure of leifite projected onto (001) (top) and (100) (bottom), as adapted from Coda *et al.* (1974). The SiO_4 tetrahedra are ruled, the BeO_4 tetrahedra are indicated by crosses, the Na atoms are shown as ruled circles, and the H_2O molecules, as open circles.

obtained by static heating tests of a bulk sample, and the 6.89 wt.% obtained by difference from the average analytical total in the electron-microprobe analyses.

According to the classification scheme of Liebau (1985), gerenite-(Y) belongs to the group of silicates with unbranched single rings of the form $[Si_6O_{18}]^{12-}$, which also includes baratovite, beryl, combeite, dioptase, imandrite, kazakovite, petarasite, scawtite, tourmaline, zirsinalite, and synthetic $Na_8Sn(Si_6O_{18})$ (Liebau 1985).

Because most gerenite-(Y) occurs intergrown with kainosite-(Y) and quartz at the type locality, and because the intergrowths may be pseudomorphic after leifite (Miller 1996, Jambor *et al.* 1998), it is interesting to compare the structure of gerenite-(Y) with those of kainosite-(Y) and leifite. The structure of kainosite-(Y), $Ca_2(Y,Ce)_2(SiO_3)_4(CO_3)\cdot H_2O$, was solved by Rumanova *et al.* (1967) and refined by Giuseppetti *et al.* (1989). They showed that the structure consists of $[Si_4O_{12}]^{8-}$ rings and CO_3 groups oriented approximately parallel to (001), and occupying "holes" in a framework made up of (Y,*REE*) and Ca polyhedra that alternately form sheets parallel to (010) (Fig. 4). Unlike gerenite-(Y), the atoms at the (Y,*REE*) positions are coordinated by eight O atoms forming a distorted dodecahedron; the mean bond-length is 2.385 Å, and the polyhedron volume is 23.57 Å^3. Like gerenite-(Y), the atoms at the Ca positions are coordinated by eight anions; however, the resulting polyhedron is a distorted dodecahedron rather than a dipyramid. The mean bond-distance is 2.385 Å, and the polyhedron volume is 23.57 Å^3; these are somewhat smaller than the corresponding values for gerenite-(Y) (2.578 Å and 26.95 Å^3, respectively). Similar to gerenite-(Y), one of the anions coordinating the Ca position is an H_2O molecule; the Ca–H_2O distance is 2.505 Å [compared to 2.374 Å in gerenite-(Y)].

The crystal structure of leifite, $Na_6Be_2Al_2Si_{16}O_{39}(OH)_2 \bullet 1.5H_2O$, was determined by Coda *et al.* (1974), who showed that there are two Si, one (Si,Al), and one Be sites, all in tetrahedral coordination with oxygen (Fig. 5). The (Si,Al) tetrahedra (occupied by approximately ⅔ Si and ⅓ Al) form six-membered rings parallel to (001). However, the centers of the rings are much farther apart (14.352 Å) than in gerenite-(Y) (~9.5 or 12.6 Å, the latter measured diagonally across the unit cell), because in leifite they are linked by Si and Be tetrahedra, which gives rise to additional chains and rings. There are H_2O molecules at the centers of the six-membered rings, and Na atoms occupy irregular seven-coordinated sites within the three-dimensional framework of Si and Be tetrahedra. Electron-microprobe analyses by Petersen *et al.* (1994) showed excess (Na,K) atoms that presumably could be accommodated in place of the H_2O molecules. Wet-chemical and infrared spectroscopic analyses by Larsen & Åsheim (1995) showed excess K atoms and no H_2O. The leifite structure was classified by Liebau (1985) as a tectosilicate, but with an interrupted (open-branched *zweier*) framework.

It is interesting to note the similarities that exist among the structures of gerenite-(Y), kainosite-(Y) (the $Ca\phi_8$ polyhedron and the H_2O position) and leifite (six-membered rings). This implies a paragenetic relationship between the three minerals, as suggested by their spatial relationship at the type locality.

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