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SERENDIBITE, A COMPLEX BOROSILICATE MINERAL FROM PONTIAC, QUEBEC: DESCRIPTION, CHEMICAL COMPOSITION, AND CRYSTALLOGRAPHIC DATA

JOEL D. GRICE§

Canadian Museum of Nature, PO Box 3443, Stn D, Ottawa, ON, K1P 6P4, Canada

PHILIPPE M. BELLEY

Department of Earth Sciences, University of Ottawa, ON, K1N 6N5, Canada

MOSTAFA FAYEK

Department of Geological Sciences, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

ABSTRACT

Serendibite has been recently discovered in the Portage-du-Fort area, Pontiac Regional County Municipality, Quebec. Dark blue, often polysynthetic twinned on {011} and with no cleavage, serendibite crystals occur exclusively in a calc-silicate rock. Fine-grained anhedral serendibite, sometimes poikiloblastic, occurs with aluminous diopside. Less commonly, serendibite may form decussate masses in the same rock type. Serendibite is biaxial negative, with indices of refraction α 1.685(2), β 1.700(2), and γ 1.712(2); $2V_{\text{meas.}} = 93.6(4)°$, $2V_{\text{calc.}} = 91°$. Orientation matrix is X ^ **c** = +20.5°, Y ^ **b** = –42.6°, and Z ^ **a** = –24.6°. Dispersion is strong, *r* << *v*, and there is no pleochroism. Serendibite is triclinic, space group $P\bar{1}$ with cell parameters refined from an X-ray powder-diffraction pattern: *a* 10.035(2), *b* 10.423(3), *c* 8.648 (2) Å, α 106.47(3)°, β 95.91(2)°, γ 124.46(2)°, *V* 674.3(2) $Å^3$. The seven strongest lines of the X-ray powder diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 3.328(45)($\bar{2}30$), 3.029 (96)(012, 021, $\bar{1}\bar{2}2$), 2.854(96)($0\bar{1}3$, $0\bar{3}1$, 120), 2.689(29)($3\bar{1}1$), 2.604(95)(030), 2.469(100)($\bar{2}\bar{1}3$, $0\bar{3}3$), and 2.357(28)($2\bar{2}3$, $2\bar{3}3$). The crystal structure determination refined to *R* = 2.1% for 3877 unique reflections. The borosilicate structure, a member of the aenigmatite-rhönite group, is composed of layers parallel to (011). Layers of tetrahedral chains cross-linked by octahedral polyhedra alternate with layers of octahedral chains cross-linked by square antiprism polyhedral sheets. Tetrahedral and octahedral polyhedra are partially ordered and site assignments were determined. All cation sites are disordered to some degree.

Keywords: serendibite, borosilicate, crystal structure, related structures, site assignment

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§ *Corresponding author; E-mail*: jgrice@mus-nature.ca

INTRODUCTION

Serendibite is a rare borosilicate known from just over a dozen occurrences worldwide, where it occurs as a metasomatic product in high-temperature environments, under a wide range of pressures. The mineral is a component of boron-bearing calc-silicate rocks hosted in marble, or in metasomatite between a silica-undersaturated rock (commonly marble) and a more siliceous rock type (such as granite, granite gneiss, K-feldspar rock, *etc*.). All occurrences formed under upper amphibolite to granulite regional metamorphic conditions with the exception of that in Riverside, California, which is a contact metamorphic aureole (Richmond 1939). The geological setting of serendibite from the Portage-du-Fort area, Quebec, resembles most other serendibite localities in the world: Melville Peninsula, Nunavut (Hutcheon *et al*. 1977), Gangapitiya, Sri Lanka (Prior & Coomaraswamy 1903), Johnsburg, New York, USA (Larsen & Schaller 1932, Grew *et al*. 1991a), Russell, New York, USA (Grew *et al*. 1990), Orange Co., New York, USA (Rader & Peck 2006), Tayozhnoye, Eastern Siberia, Russia (Grew *et al*. 1991b), Lanapera and Ihosy, Madagascar (Nicollet 1990a, 1990b), Handeni district, Tanzania (Bowden *et al*. 1969), Bug region, Ukraine (Yaroshchuk *et al*. 1990), and Mogok, Burma (Themelis 2008).

The crystal structure of serendibite was first solved by Buerger & Ventkatakrishnan (1974) and more recently refined by Van Derveer *et al*. (1993). The cation distribution at the various sites is questionable for both determinations. The major portion of the study of this occurrence at Pontiac, Quebec, involves the determination of the genesis of this formation. It is discussed in detail in an accompanying paper by Belley *et al*. (in prep.). Here we confine our discussion to a full description, with new data, for serendibite.

GEOLOGICAL SETTING AND OCCURRENCE

The serendibite occurrence is located in the Portage-du-Fort area, Pontiac Regional County Municipality, Quebec, a short distance north of the Ottawa River, 80 kilometers west of Ottawa, Ontario. The occurrence was discovered in 2011 by mineral collector Mike Irwin.

The serendibite-bearing calc-silicate rock is hosted in serpentine- and dolomite-bearing marbles of the Portage-du-Fort Group, described by Brun (1984), in the Late Proterozoic Central Metasedimentary Belt (CMB), Grenville Province – a series of metasediments (carbonate and siliciclastic sediments) and possibly metavolcanic rocks (amphibolite) metamorphosed to upper amphibolite facies with localized granulite conditions. These rocks are intruded by weakly metamorphosed gabbros and various granitoids (Hocq 1994). The CMB consists of a monocyclic allochtonous terrane (Hocq 1994) that is probably, based on interpretations stemming from Nd isotope evidence, the northern termination of a failed back-arc rift in a continental margin setting (Dickin & McNutt 2007). The Portage-du-Fort Group occurs in the southwest part of the Marble Domain described by Corriveau & van Breeman (2000). Peak metamorphic conditions are reported to be consistent throughout the nearby Otter Lake area at 650–700 °C and 6 ± 1 kbar (Perkins *et al*. 1982) and 700 ± 50 ˚C and 7 ± 0.5 kbar (Kretz 2009).

MINERAL DESCRIPTION

General appearance and physical properties

Dark blue, often polysynthetically twinned on {011} and with no cleavage, serendibite crystals occur exclusively in a calc-silicate rock (Fig. 1). Fine-grained anhedral serendibite, sometimes poikiloblastic, occurs with aluminous diopside. Less commonly, serendibite may form decussate masses in the same rock type. On occasion, serendibite-diopside symplectite and diopside coronas rim serendibite grains. Calcite-filled pockets in the calc-silicate rock contain euhedral serendibite crystals up to 4 cm in size. A significant proportion of serendibite is replaced by a high-temperature alteration assemblage of tourmaline (uvite) with lesser spinel and calcite. Serendibite in calcite pockets is the most significantly altered, but crystals showing minimal alteration (*e.g*., a thin rind of uvite alteration) occur rarely. Serendibite crystals in the calcite pockets are, at times, intergrown with or enveloped by phlogopite crystals with the basal plane of phlogopite parallel to the long axis of the serendibite crystals. This elongate axis lies within the twin plane {011}, but the orientation of twin plane relative to phlogopite overgrowths could not be determined.

FIG. 1. Uvite, spinel, and calcite pseudomorph after serendibite, 25 × 14 × 12 mm crystal, showing dissolution along twin planes. The orientation of the twin plane is parallel to the long axis of the crystal.

Optical Properties

An optical study was undertaken using thin sections, grain mounts, and a single crystal mounted on a spindle stage. The Pontiac serendibite is pale blue in transmitted light, with low birefringence, strong dispersion $r << v$, and no visible pleochroism, the latter being uncharacteristic compared to serendibite from other localities. Using a spindle stage and extinction curves described by Bloss (1981) and calculated with the EXCALIBR program (Gunter *et al.* 2004) we obtained the following results: biaxial negative, α 1.685(2), β 1.700(2), and γ 1.712(2); $2V_{meas.} = 93.6(4)^\circ$ by extinction curves, $2V_{meas.} = 85^\circ$ by the Kamb method, and $2V_{calc.} = 91^\circ$. Measurements were made using a filter that transmits light with a wavelength of 590 nm. The crystal used for determining the extinction curves was mounted on a single crystal diffractometer to obtain the orientation matrix relating optic axes to crystallographic axes; their relationships are $X \wedge \mathbf{c} = +20.5^\circ$, $Y \wedge \mathbf{b} = -42.6^\circ$, and $Z \wedge \mathbf{a} = -24.6^\circ$.

Chemical composition

The chemical compositions were obtained with a JEOL 8230 electron microprobe operating in wavelength-dispersion (WD) mode. Data reduction was done with a standard ZAF correction. The operating voltage was 20 kV, the beam current was 20 nA, and the beam diameter was 5 μm. The following standards were used: sanidine (K*K*α), diopside (Ca*K*α), fluorite (F*K*α), sphalerite (Zn*L*α), rutile (Ti*K*α), baryte (Ba*L*α), hematite (Fe*K*α, tephroite (Mn*K*α), albite (Na*K*α), and tugtupite (Cl*K*α). Several 100-s energy-dispersion (ED) scans were made, and indicated no elements with Z > 8, other than those reported here. Data for all elements in the samples were collected for 20 to 25 s. The chemical analyses are from two averaged datasets from separate samples, in which several grains were analyzed (Table 1).

The B concentration analysis was done with a Cameca IMS 7f secondary ion mass spectrometer (SIMS) at the University of Manitoba using a primary O^- beam with a 15 μm beam, a sample accelerating voltage +10kV, electrostatic analyzer +10 kV, and Balzers SEV 1217 detector (Table 2). An elbaite tourmaline standard was used as a B concentration standard (B_2O_3 = 10.1 wt.%, No. 98114, Dyer *et al.* 2001). Based on these data, the average chemical composition of the two analyses (Table 1) is: SiO_2 22.95, TiO_2 0.06, Al_2O_3 36.23, B_2O_3 7.51, FeO 1.80, MnO 0.05, ZnO 0.02, MgO 14.68, CaO 15.30, BaO 0.00, Na_2O 0.36, K_2O 0.00, F 0.01, and Cl 0.01, for a total of 98.98 wt.%. The empirical formula based on 20 anions is: $Ca_{1.93}Na_{0.08}Mg_{2.58}Al_{5.03}B_{1.53}Si_{2.71}O_{20}$. The B concentrations obtained by SIMS will be compared to structural refinement data.

Boron isotopes

Boron isotopes were determined at the same time, and therefore with the same conditions, as the B analysis (Table 2). Boron isotopes are expressed in delta notation as per mil deviation from boric acid standard NIST SRM 951 ($^{11}B/^{10}B = 4.0437 \pm 0.0033$, Catanzaro *et al.* 1970). The average of seven spot determinations from two crystal fragments from one sample are $\delta^{11}B$ (‰) +7.4 (max.), +2.2 (min), +4.3(1.1) (average). The analytical procedure was similar to that of Chaussidon & Albarède (1992). Instrumental mass fractionation (IMF) and analytical quality were assessed by replicate analyses of a serendibite reference material (No. 5265A, $^{11}B/^{10}B = 4.0365 \pm 0.0053$, Leeman & Tonarini 2001; repeatability on reference material was 0.3‰). Precision for unknown samples was ±0.3‰ (1σ).

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction

X-ray powder diffraction data (XRPD) for serendibite were collected with a Siemens D5000 powder diffractometer using Cu radiation (λ = 1.5418 Å) with a scintillation detector and a graphite monochromator, operating at 40kV / 40mA, and calibrated according to Rowe (2009). Data was collected from 3–80° 2θ using a step-width of 0.02° 2θ and a dwell time of 2s/step. Divergence and anti-scatter slits were both set to 1 mm. The X-ray diffraction data are given in Table 3. The unit cell parameters obtained by refining the X-ray powder diffraction data are essentially the same as those derived from the crystal structure determination. Indexing of the XRPD was difficult due to the low symmetry and triclinic crystal system, compounded by the overlap of reflections due to similar *a* and *b* cell parameters. To alleviate some of these difficulties, the XRPD pattern was calculated (Kraus & Nolze 1996) using the crystal structure refined from the same material. The I_{calc} was used (Rowe *et al.* 2013) to eliminate many possible overlaps, as there are many reflections that would not have sufficient intensity to be observed on a powder diffraction pattern.

Crystal-structure determination

The single crystal of serendibite used for the collection of X-ray intensity data was a thin plate measuring 120 × 100 × 20 μm. Intensity data were collected with a fully-automated Bruker D8 three-circle diffractometer equipped with a rotating anode generator operating at, 50 kV, 24 mA, with graphite-monochromated Mo*K*α radiation, multi-layer optics, and an APEX-II CCD detector. This arrangement yields a very intense X-ray beam. A full sphere of intensity data was collected up to $2\theta = 60^\circ$ using 6 s frames at frame widths of 0.2°.

TABLE 1. SERENDIBITE: ANALYTICAL DATA

Sample	10	24	Structure analysis		10	24	Structure analysis
N	5	8					
	wt.%				Ions per 20 anions		
SiO_2	23.47	23.89	24.57	Si	2.763	2.780	2.83
TiO_2	0.06	0.04		Ti	0.005	0.004	
Al_2O_3	35.70	36.36	35.65	Al	4.954	4.987	4.84
FeO	1.81	1.80		Fe	0.178	0.175	
MnO	0.04	0.05		Mn	0.004	0.005	
ZnO	0.01	0.01		Zn	0.001	0.001	
MgO	14.57	14.76	15.90**	Mg	2.557	2.561	2.73**
CaO	15.55	15.27	15.39	Ca	1.962	1.904	1.90
Na_2O	0.34	0.36	0.45	Na	0.078	0.081	0.10
K_2O	0.01	0.00		K	0.002	0.000	
BaO	0.01	0.01		Ba	0.000	0.000	
B_2O_3	7.51*	7.51*	8.05	B	1.526	1.508	1.60
F	0.00	0.02		F	0.000	0.007	
Cl	0.01	0.00		Cl	0.002	0.000	
O=F, Cl	0.00	–0.01					
Total	99.09	100.07	100				

*Assumed value based on part of sample 10: B_2O_3 = 7.51 ± 0.09 wt.% (SIMS).
** Total Fe
Empirical formula: $Ca_{1.93}Na_{0.08}Mg_{2.56}Al_{4.97}B_{1.52}Si_{2.77}O_{20}$
Structural formula: $(Ca_{1.93}Na_{0.08})_{\Sigma 2.01}(Al_{3.44}Mg_{2.56})_{\Sigma 6}(Si_{2.77}B_{1.52}Al_{1.53})_{\Sigma 5.82}O_{20}$
Formula from structure determination $(Ca_{1.90}Na_{0.10})_{\Sigma 2}(Al_{3.27}Mg_{2.73})_{\Sigma 6}(Si_{2.83}B_{1.60}Al_{1.57})_{\Sigma 6}O_{20}$

TABLE 2. SERENDIBITE: BORON ISOTOPE ANALYSIS

Primary ion beam (O^-)	~ 5 nA accelerated at 12.5 kV
Spot size	~ 15 µm
Sample accelerating voltage	+10 kV
Electrostatic analyzer in secondary column	+10 kV
Entrance slit	53.8
Mass resolving power	800
Detector	Balzers SEV 1217 electron multiplier coupled with an ion counting system
Deadtime	37 s
Species detected	^{11}B, ^{10}B, ^{30}Si
Analysis	50 cycles, ~5 minutes
Pre-sputter	60 s
Offset	0 V
Spot to spot reproducibility on elbaite std.	σ = 0.2‰

With these operating conditions, no deterioration in the degree of crystallinity was evident in the final analysis of the reflections used as intensity standards. Information relevant to the data collection and structure determination is given in Table 4. The three-dimensional data were corrected for Lorentz, polarization, and background effects, and a multiple-measured reflection was averaged using the Bruker program SAINT. An empirical absorption correction was applied (SADABS, Sheldrick 1998), which reduced the internal residual for merging data from 6.16% before the absorption correction to 3.01% after the absorption correction (for certain reflections), and the *R*(int) for all reflections merged is 2.19%. All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors of neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.935, which suggests the centrosymmetric space group $P\bar{1}$.

For easy comparison, the starting model for the refinement kept the site assignments and labels of Van Derveer *et al.* (1993). Note that the original structure determination by Buerger & Ventkatakrishnan (1974) had a different setting, corresponding to the standard, smallest unit cell with cell parameters $a < b < c$ and angles α, β, γ all acute. This gave 8.63, 9.532, 10.019 Å, 64.17°, 83.94°, 65.29° with V = 670.94 Å^3. The cell was reoriented by Machin & Suesse (1974) to coincide with the setting of the aenigmatite group, of which it is a member.

The addition of an isotropic extinction correction improved the refinement considerably, attesting to the perfection of the crystal. There was no evidence of twinning in the data collection, but there was evidence of very small adhering second crystal that bore no crystallographic relationship to the major phase. The maximum and minimum electron densities in the final

TABLE 3. X-RAY POWDER DIFFRACTION DATA

d_{obs}	$d_{calc.}$	I_{obs}	I_{calc}	*hkl*		d_{obs}	$d_{calc.}$	I_{obs}	I_{calc}	*hkl*	
7.793	7.801	13	10.6	100	*	2.115	2.115	9	12.3	$0\bar{1}4$	*
7.190	7.236	8	19.6	$0\bar{1}\bar{1}$	*	2.065	2.065	6	8.0	$\bar{1}04$	*
4.654	4.643	6	17.3	011	*	2.040	2.041	69	85.6	$\bar{2}04$	*
4.083	4.074	11	11.0	$\bar{2}01$	*		2.038		87.0	$2\bar{5}1$	
	3.901		1.8	200		2.031	2.036	60	12.2	$4\bar{4}2$	
3.913	3.901	6	8.7	$\bar{2}11$		2.115	2.115	9	12.3	$0\bar{1}4$	*
3.617	3.618	15	24.6	$0\bar{2}2$	*	2.026	2.025	47	100	$4\bar{1}1$	*
	3.330		56.6	$\bar{2}12$		1.985	1.985	7	5.9	$\bar{5}31$	*
3.328	3.326	45	43.4	$\bar{2}30$		1.955	1.955	6	3.5	004	*
3.148	3.161	9	14.7	$\bar{3}11$			1.953		2.5	040	
	3.145		1.8	$\bar{1}\bar{2}1$		1.924	1.924	18	24.2		*
	3.105		14.8	102			1.922		24.8		
3.105	3.102	16	15.6	$2\bar{2}2$		1.895	1.895	10	3.1	$\bar{2}\bar{2}4$	
	3.102		10.8	$\bar{2}\bar{1}1$			1.895		3.5	$\bar{3}04$	
3.029	3.027	30	34.2	012		1.874	1.874	7	20.4	$\bar{4}42$	*
	3.026		37.8	021		1.845	1.842	9	10.5	023	
	2.989		7.2	$\bar{1}\bar{2}2$			1.842		10.0	032	
2.986	2.983	6	9.1	$3\bar{2}1$		1.814	1.815	9	10.3	$\bar{4}33$	
2.896	2.895	11	24.3	$3\bar{3}1$	*		1.814		9.3	$\bar{4}51$	
2.854	2.855	96	81.2	$0\bar{1}3$		1.725	1.724	8	6.1	320	
	2.852		88.3	$0\bar{3}1$			1.724		5.6	$\bar{4}\bar{1}3$	
	2.852		25.2	120		1.697	1.698	7	8.3	$\bar{2}\bar{3}4$	
2.823	2.820	29	31.0	$\bar{2}22$			1.698		8.0	$2\bar{5}4$	
	2.819		40.2	$\bar{2}31$		1.675	1.673	9	9.6	$\bar{5}33$	
2.768	2.764	7	5.4	$0\bar{2}3$			1.672		5.6	$0\bar{5}1$	
	2.762		8.9	$0\bar{3}2$		1.628		5			
2.715	2.715	10	15.4	$\bar{3}31$	*	1.585	1.584	15	25.6	$0\bar{4}5$	
2.689	2.689	29	52.0	$3\bar{1}1$	*		1.584		23.8	$0\bar{5}4$	
2.604	2.605	95	85.6	030	*	1.563	1.563	17	17.9	$\bar{2}15$	*
2.570	2.570	7	15.2	$1\bar{1}3$	*	1.553	1.551	14	25.1	402	*
	2.471		13.0	$\bar{1}13$		1.500	1.501	13	16.1	$\bar{6}23$	*
2.469	2.471	100	69.2	$\bar{2}\bar{1}3$		1.448	1.448	38	46.1	$\bar{6}13$	*
	2.412		16.3	$0\bar{3}3$		1.438	1.437	23	51.7	$\bar{4}53$	*
2.394	2.392	16	22.2	211		1.428	1.428	40	52.7	$2\bar{5}1$	
	2.391		17.9	202			1.426		54.2	240	
	2.354		24.7	$\bar{2}\bar{2}1$		1.360	1.360	5	2.5	$\bar{3}\bar{4}3$	
2.357	2.355	28	24.5	$2\bar{2}3$			1.359		3.4	$\bar{6}01$	
	2.355		12.5	$2\bar{3}3$		1.311		9			
2.253	2.254	12	7.2	$1\bar{4}0$	*	1.299		4			
2.222	2.222	7	3.1	$\bar{3}41$		1.285	1.284	5	6.0	$\bar{4}\bar{1}6$	*
	2.220		4.0	$4\bar{4}1$		1.269	1.269	8	2.0	$\bar{7}53$	*
2.168	2.167	11	5.2	$\bar{2}23$		1.250	1.250	6	3.0	$\bar{8}51$	*
	2.167		6.8	$\bar{2}\bar{2}3$		1.223	1.222	5	3.7	$\bar{8}52$	*
2.141	2.141	4	2.0	$0\bar{4}2$	*	1.215	1.215	4	1.4	$\bar{8}31$	*

*Reflections used in cell refinement.
Cell parameters from the refinement: *a* 10.035(2), *b* 10.423(3), *c* 8.648 (2) Å, α 106.47(3)°, β 95.91(2)°, γ 124.46(2)°, *V* 674.3(2) Å^3

cycle of refinement were +0.60 and –0.57 $e^{-}/Å^3$. With all atoms located and assigning anisotropic displacement factors, the structure refined to $R = 2.12\%$. The final positional and anisotropic displacement parameters of atoms are given in Table 5 and selected bond lengths and angles in Table 6. Tables listing the observed and calculated structure factors and a .cif file may be obtained from the Depository of Unpublished Data, on the MAC website [serendibite CM52_1].

Description of the Structure

Serendibite has a layered borosilicate structure (Fig. 2) with 'tetrahedral layers' interleaved with

TABLE 4. DATA COLLECTION AND STRUCTURE REFINEMENT INFORMATION

Space Group	$P\bar{1}$(SG # 2)	Measured reflections	7869
a (Å)	10.022(7)	Unique reflections	3877
b (Å)	10.406(7)	Observed reflections [>4σ(*F*)]	3833
c (Å)	8.643(5)	*R*(int) (%)	0.97
α (°)	106.41(6)	Goodness of fit on F^2	1.11
β (°)	95.992(6)	*R* index (%) for all data	2.12
γ (°)	124.38(8)	wR_2 (%) for all data	5.39
V (Å^3)	672.7(1.4)	Refinement by full-matrix least squares on F^2	
Ideal unit-cell contents: $Ca_4Mg_4Al_8O_8(Si_8B_4Al_2O_{32})$ μ = 1.79 mm^{-1}			

TABLE 5. SERENDIBITE ATOMIC COORDINATES AND ANISOTROPIC DISPLACEMENT FACTORS (Å^3)

Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}
B1*	0.46493(4)	0.23511(4)	0.32967(5)	0.0092(1)	0.0075(1)	0.00727(1)	0.0028(1)	0.0024(1)	0.00551(8)	0.00789(8)
Si2	0.98328(2)	0.22742(2)	0.34099(2)	0.00743(5)	0.00740(5)	0.00692(7)	0.00300(5)	0.00187(5)	0.00432(4)	0.00748(4)
Al3^{IV}	0.78548(2)	0.34413(2)	0.23250(3)	0.00648(6)	0.00599(6)	0.00577(7)	0.00254(5)	0.00151(6)	0.00369(5)	0.00623(4)
B4*	0.26955(8)	0.33018(8)	0.21973(9)	0.0078(2)	0.0070(2)	0.0060(2)	0.0033(2)	0.0021(2)	0.0034(2)	0.0076(2)
Al5^{IV}	0.64358(2)	0.94376(2)	0.44299(3)	0.00842(5)	0.00860(5)	0.00942(7)	0.00189(5)	0.00282(5)	0.00507(4)	0.00949(4)
Si6	0.35643(2)	0.55472(2)	0.05380(2)	0.00695(5)	0.00678(5)	0.00629(7)	0.00226(5)	0.00227(5)	0.00423(4)	0.00682(4)
Al1	0	0	½	0.00644(8)	0.00646(8)	0.0054(1)	0.00224(7)	0.00160(8)	0.00410(6)	0.00617(6)
Al2	0	½	0	0.00621(8)	0.00596(8)	0.0060(1)	0.00226(7)	0.00233(8)	0.00368(6)	0.00615(6)
Al3	0.31186(2)	0.85618(2)	0.17249(3)	0.00644(6)	0.00921(6)	0.00718(7)	0.00380(5)	0.00278(6)	0.00513(5)	0.00729(4)
Al4	0.77825(2)	0.82278(2)	0.14588(3)	0.00765(6)	0.00875(6)	0.00810(8)	0.00375(5)	0.00306(6)	0.00533(5)	0.00791(4)
Mg5	0.09510(2)	0.94408(3)	0.06183(3)	0.00494(6)	0.00678(6)	0.00627(8)	0.00414(6)	0.00289(6)	0.00400(5)	0.00527(5)
Mg6	0.59376(3)	0.93924(3)	0.05705(3)	0.00438(7)	0.00672(7)	0.00762(9)	0.00423(6)	0.00243(6)	0.00346(5)	0.00585(5)
Al7	0.99861(2)	0.74106(2)	0.25869(3)	0.00683(6)	0.00612(6)	0.00609(8)	0.00234(5)	0.00222(6)	0.00411(5)	0.00635(5)
Ca8*	0.21478(2)	0.62399(2)	0.39756(2)	0.01225(5)	0.01154(4)	0.00972(6)	0.00551(4)	0.00485(4)	0.00824(3)	0.01022(3)
Ca9*	0.64807(2)	0.60219(2)	0.38291(2)	0.00732(5)	0.01222(5)	0.01256(6)	0.00626(4)	0.00317(4)	0.00444(3)	0.01147(4)
O1	0.35267(6)	0.06425(6)	0.17242(7)	0.0105(2)	0.0116(2)	0.0107(2)	0.0034(1)	0.0027(2)	0.0076(1)	0.0109(1)
O2	0.84330(6)	0.04817(6)	0.16745(6)	0.0107(2)	0.0108(1)	0.0079(2)	0.0036(1)	0.0034(1)	0.0072(1)	0.0096(1)
O3	0.54009(7)	0.95434(7)	0.28672(8)	0.0127(2)	0.0125(2)	0.0148(2)	0.0015(2)	0.0054(2)	0.0068(1)	0.0151(1)
O4	0.01507(6)	0.93475(6)	0.27690(6)	0.0087(1)	0.0079(1)	0.0075(1)	0.0028(1)	0.0035(1)	0.0046(1)	0.0084(1)
O5	0.24008(6)	0.86637(6)	0.38013(7)	0.0097(2)	0.0092(1)	0.0096(2)	0.0033(1)	0.0016(2)	0.0053(1)	0.0101(1)
O6	0.76330(6)	0.88112(6)	0.38216(7)	0.0077(2)	0.0086(1)	0.0110(2)	0.0041(1)	0.0021(1)	0.0047(1)	0.0095(1)
O7	0.49056(6)	0.21044(6)	0.49464(7)	0.0131(2)	0.0116(2)	0.0138(2)	0.0062(1)	0.0079(2)	0.0063(1)	0.0131(1)
O8	0.95735(6)	0.78823(6)	0.48137(6)	0.0085(1)	0.0078(1)	0.0103(2)	0.0041(1)	0.0028(1)	0.0049(1)	0.0089(1)
O9	0.90003(6)	0.32666(6)	0.38039(7)	0.0146(2)	0.0117(2)	0.0089(2)	0.0043(1)	0.0036(2)	0.0094(1)	0.0110(1)
O10	0.38423(6)	0.32646(6)	0.34502(7)	0.0100(2)	0.0110(2)	0.0092(2)	0.0044(1)	0.0014(2)	0.0057(1)	0.0108(1)
O11	0.65067(6)	0.16270(6)	0.04627(7)	0.0091(2)	0.0108(2)	0.0117(2)	0.0041(1)	0.0037(2)	0.0062(1)	0.0106(1)
O12	0.16086(6)	0.17655(6)	0.06163(7)	0.0087(2)	0.0078(1)	0.0082(2)	0.00102(1)	0.00008(1)	0.0049(1)	0.0093(1)
O13	0.53770(6)	0.71128(6)	0.04842(7)	0.0136(2)	0.0114(2)	0.0112(2)	0.0040(1)	0.0048(2)	0.0083(1)	0.0118(1)
O14	0.06852(6)	0.72596(6)	0.06336(6)	0.0095(1)	0.0085(1)	0.0078(1)	0.0035(1)	0.0027(1)	0.0057(1)	0.0085(1)
O15	0.24043(6)	0.61578(6)	0.11701(6)	0.00880(1)	0.0107(1)	0.0083(2)	0.0037(2)	0.0030(1)	0.0063(1)	0.0092(1)
O16	0.75362(6)	0.61410(6)	0.13551(7)	0.00837(2)	0.0100(2)	0.0081(2)	0.0018(1)	0.0026(2)	0.0041(1)	0.0105(1)
O17	0.39002(6)	0.48764(6)	0.19354(6)	0.0099(2)	0.0082(1)	0.0097(2)	0.0048(1)	0.0033(1)	0.0052(1)	0.0092(1)
O18	0.95140(6)	0.52591(6)	0.21501(7)	0.0105(2)	0.0106(2)	0.0090(2)	0.0045(1)	0.0029(2)	0.0065(1)	0.0099(1)
O19	0.16629(6)	0.35950(6)	0.31304(7)	0.0114(2)	0.0098(2)	0.0121(2)	0.0040(1)	0.0069(2)	0.0057(1)	0.0115(1)
O20	0.65566(6)	0.36844(6)	0.33290(7)	0.0179(2)	0.0172(2)	0.0104(2)	0.0048(1)	0.0055(2)	0.0136(1)	0.0136(1)

*Site occupancy factors: B1 = 0.622(1), Si1 = 0.378; B4 = 0.976(1), Si4 0.024;
Ca8 = 0.9457(6), Na8 = 0.0542, Ca9 = 0.9526(6), Na9 = 0.0474
Al^{IV} in [4]-fold coordination

TABLE 6. SERENDIBITE SELECTED BOND DISTANCES (Å)

Ca8–O7	2.309(2)	Ca9–O17	2.307(2)	Mg5–O1	2.075(2)	Mg6-O11	1.999(2)
Ca8–O19	2.372(2)	Ca9–O10	2.373(2)	Mg5–O12	2.081(2)	Mg6–O2	2.034(2)
Ca8–O18	2.383(2)	Ca9–O20	2.394(2)	Mg5–O4	2.106(1)	Mg6–O13	2.082(2)
Ca8–O9	2.417(2)	Ca9–O8	2.413(2)	Mg5–O12*	2.119(2)	Mg6–O11*	2.092(2)
Ca8–O5	2.439(2)	Ca9–O6	2.446(2)	Mg5–O14	2.135(2)	Mg6–O3	2.097(2)
Ca8–O15	2.448(2)	Ca9–O10*	2.460(2)	Mg5–O2	2.146(2)	Mg6–O1	2.104(2)
Ca8–O20	2.504(2)	Ca9–O16	2.486(2)	<Mg5–0>	<2.110>	<Mg6–O>	<2.068>
Ca8–O9*	2.857(2)	Ca9–O19	2.842(2)				
<Ca8–O>	<2.466>	<Ca9–O>	<2.465>				
Al1–O4	1.908(1) x 2	Al3–O3	1.889(2)	Al4–O13	1.932(2)	Al7–O4	1.885(2)
Al1–O6	1.914(2) x 2	Al3–O14	1.934(2)	Al4–O12	1.954(1)	Al7–O14	1.894(1)
Al1–O8	1.946(2) x 2	Al3–O11	1.943(1)	Al4–O4	1.960(2)	Al7–O18	1.915(2)
<Al1–O>	<1.923>	Al3–O1	1.964(2)	Al4–O2	1.990(2)	Al7–O5	1.947(2)
		Al3–O5	2.000(1)	Al4–O6	2.007(2)	Al7–O16	1.976(2)
Al2–O14	1.916(2) x 2	Al3–O15	2.056(2)	Al4–O16	2.016(2)	Al7–O8	1.994(1)
Al2–O15	1.950(2) x 2	<Al3–O>	<1.964>	<Al4–O>	<1.977>	<Al7–O>	<1.935>
Al2–O18	1.954(2) x 2						
<Al2–O>	<1.940>						
B1–O1	1.527(1)	Si2–O9	1.647(1)	Al3–O11	1.711(1)	B4–O12	1.448(1)
B1–O7	1.539(1)	Si2–O2	1.650(1)	Al3–O20	1.730(1)	B4–O19	1.485(1)
B1–O10	1.547(1)	Si2–O19	1.657(1)	Al3–O18	1.740(1)	B4–O17	1.492(1)
B1–O20	1.597(1)	Si2–O8	1.673(1)	Al3–O9	1.745(1)	B4–O10	1.520(1)
<B1–O>	<1.553>	<Si2–O>	<1.656>	<Al3^{IV}–O>	<1.732>	<B4–O>	<1.486>
Al5–O3	1.683(1)	Si6–O13	1.635(1)				
Al5–O7	1.696(1)	Si6–O17	1.648(1)				
Al5–O5	1.709(1)	Si6–O16	1.671(1)				
Al5–O6	1.721(1)	Si6–O15	1.680(1)				
<Al5^{IV}–O>	<1.702>	<Si6–O>	<1.658>				

'octahedral layers' oriented parallel to (011). The 'tetrahedral' layer is primarily composed of tetrahedra, but contains an octahedral polyhedron as well. Similarly the 'octahedral' layer is mainly composed of octahedra, but also contains a square antiprism polyhedron. Both layers have a considerable volume of open space, particularly the tetrahedral layer. Serendibite is a member of the aenigmatite-rhönite mineral group. The chemical substitutions in this group are discussed in detail by Kunzmann (1999).

Tetrahedral layer

There are six tetrahedral sites in the serendibite crystal structure. The tetrahedra form open-branched vierer single chains that compare well with those in the structures of other aenigmatite group minerals (Fig. 3). The chains run parallel to the **a**-axis in the (011) plane and are cross-linked into a layer by octahedral [AlO_6] polyhedra (Fig. 4). Silica, B, and Al occupy the tetrahedral sites; these sites are not well ordered. On the basis of cation size, it is likely that B (0.11 Å) and Si (0.26 Å) substitute for each other, as do Al (0.39 Å) and Si (0.26 Å), but not B (0.11 Å) and Al (0.39 Å). The lack of complete ordering presents a challenge to cation site assignments. The method used for site assignment is that outlined in Johnsen & Grice (1999) for eudialyte-group species. For each site, the following data are necessary; the number of electrons per formula unit (*epfu*), the average bond length, and the bond valence sum (BVS). Using linear equations one can determine the proportions of each pair of cations. In these calculations the ionic radius used for O^{2-} is 1.376 Å, the weighted mean of the 20 oxygen atoms with four O^{2-III} and sixteen O^{2-IV} (Table 7). The validity of the cation proportions can be verified by the agreement of electron sum *versus epfu* and BVS *versus* valence sum. All six tetrahedral sites have mixed site occupancies, but Si2, B4, and Si6 are largely ordered. The B1 site and the two Al-dominant positions, Al3^{IV} and Al5^{IV}, have almost equal proportions of a second cation. In the tetrahedral chain there are no Al tetrahedra sharing vertices and the same is true for Si. The two B tetrahedra do share a vertex. In the tetrahedral layer there are two types of S-shaped voids (Fig. 4); each is composed of 8 tetrahedra and 2 octahedra, but the types of tetrahedra differ in the two sets. In each S-void there is an O site

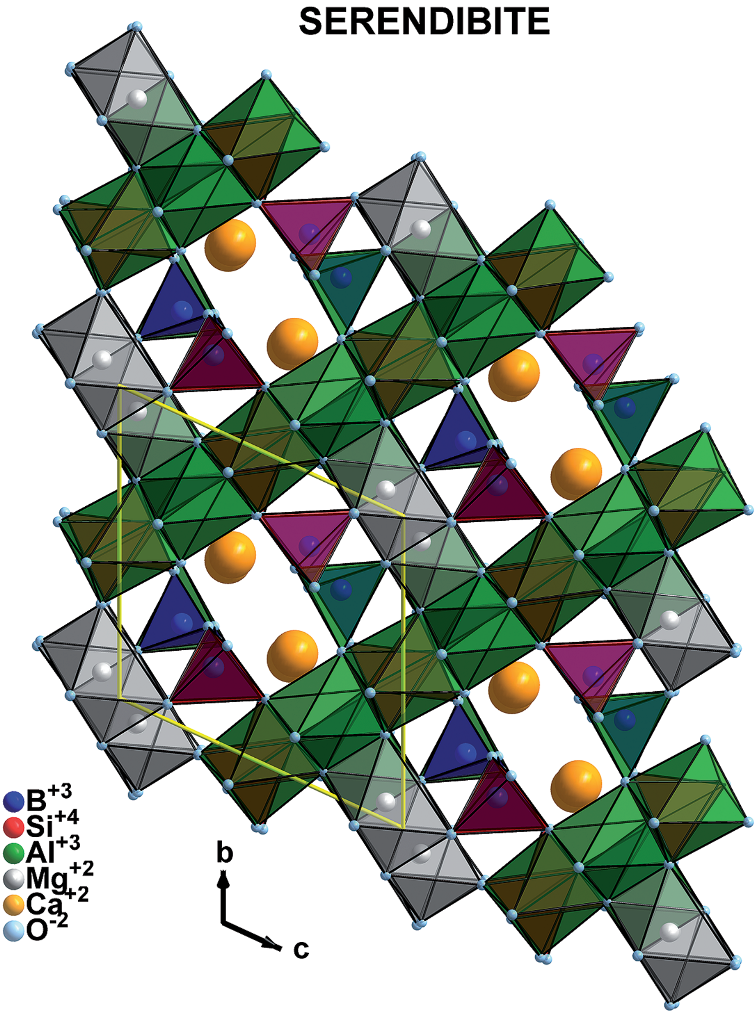

FIG. 2. Serendibite layered structure.

that points into the void. Both of these O-sites are under-bonded; O3 1.69 *vu* and O13 1.77 *vu* (Table 7).

Ca, Mg, and Al polyhedra

The two Ca sites have eight-fold coordination in a square antiprism, [CaO_8] polyhedron (Fig. 5). Of the eight bond lengths, seven are close to 2.4 Å, while the eighth is considerably longer at 2.8 Å. Van Derveer *et al*. (1993) did not include the more distant bond, giving a [CaO_7] polyhedron (a mono-capped octahedron) but we feel the long bond, with 0.09 *vu* contribution, is significant and cannot be ignored. The two Ca sites are not quite equivalent in refined *epfu* (Table 7). The square antiprisms are edge-sharing (Fig 6), forming a single chain parallel to the **a**-axis.

There are six octahedral sites in the 'octahedral layer'. Note that the Al1 octahedron is in the 'tetrahedral layer'. The average bond length calculations were used for site assignments at octahedral sites, as the scattering powers of Mg and Al are too similar, whereas the ionic radii are sufficiently different (0.535 Å for Al and 0.72 Å for Mg) to enable a reliable site assignment calculation. The two Mg sites are well ordered, but the five Al-dominant sites have a considerable amount of Mg substitution. In Table 7 our site occupancy assignments are compared with those of determined by Buerger & Ventkatakrishnan (1974) and Van Derveer *et al*. (1993). The comparison is discussed below.

The octahedra form bands or broad chains that also run parallel to the **a**-axis .The core of the band is a chain of edge-sharing Mg-centered octahedra decorated on either site by broken chains of edge-sharing Al-centered octahedra. These broad octahedral bands are cross-linked by the square antiprism chains (Fig. 6). In the octahedral layer, there are voids as well; again, two types: 4-sided and 8-sided. The significance of these voids is also discussed below.

DISCUSSION

It is of interest to compare the chemical composition of serendibite as determined by electron microprobe and SIMS analysis with that determined by crystal structure analysis. Table 1 tabulates the comparison. Of particular note is the boron analysis. Hawthorne & Grice (1990) detail the application of structure analysis for light element determination. In this study we have a SIMS analysis for boron, and it is 6.6% lower than that determined by the crystal structure analysis. As this is within error for both techniques, we consider it a good match. As for the other major cations determined by bond length calculations, the fit is even better, with a total error (microprobe plus bond length errors) of 3% or less.

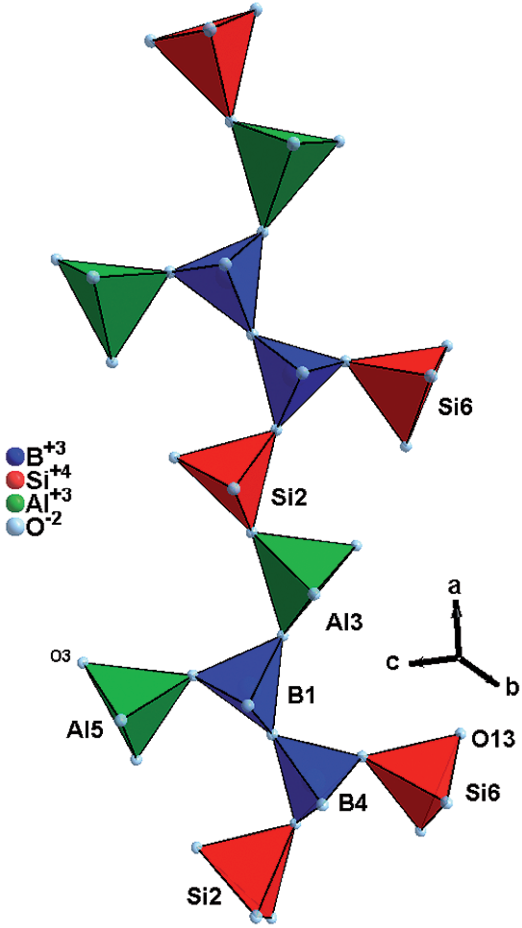

FIG. 3. Serendibite tetrahedral chain.

The boron isotope results for both uvite and serendibite are discussed in detail by Belley *et al.* (in prep.). The serendibite analysis of $\delta^{11}B$ +4.3‰ is a little more than $\delta^{11}B$ +1.9‰ for that measured from the Johnsburg, New York serendibite. The B isotope composition of serendibite is attributed to a marine evaporite source, where fourfold B coordination in serendibite contributed to a significant (~ 6.3‰) decrease of B isotopic signature (Belley *et al.* in prep).

In previous structure determinations, cation site assignments have met with only moderate success. Buerger & Ventkatakrishnan (1974) chose rather odd site substitutions, Ca/Mg and Al/B', which cannot be supported as likely. They did, however, fix the site occupancies to match the measured chemical composition. On the other hand, Van Derveer *et al.* (1993) chose much more likely site substitutions, Mg/Al and Si/B, but their final structural formula does not match the chemical analysis very well: the structure analysis gives $(Ca_{1.60}Na_{0.40})_{\Sigma 2}(Al_4Mg_2)_{\Sigma 6}(Si_{3.37}B_{1.63}Al_{1.0})_{\Sigma 6}O_{20}$ *versus* $(Ca_{1.76}Na_{0.12})_{\Sigma 1.88}(Al_{3.27}Mg_{2.64})_{\Sigma 5.91}(Si_{2.85}B_{1.69}Al_{1.46})_{\Sigma 6}O_{20}$ from chemical analysis. In the present paper, we have used a variety of methods to achieve a closer agreement between the chemical formula from the analysis and the structure derived formula: $(Ca_{1.93}Na_{0.08})_{\Sigma 2.01}(Al_{3.44}Mg_{2.56})_{\Sigma 6}(Si_{2.77}B_{1.52}Al_{1.53})_{\Sigma 5.82}O_{20}$ *versus* $(Ca_{1.90}Na_{0.10})_{\Sigma 2}(Al_{3.27}Mg_{2.73})_{\Sigma 6}(Si_{2.83}B_{1.60}Al_{1.57})_{\Sigma 6}O_{20}$. With improved site assignments, one may better understand the degree of cation ordering within the aenigmatite group of minerals. It is evident from Table 7 that the degree of ordering in serendibite is much lower than previously thought. Buerger & Ventkatakrishnan (1974) rationalized their site occupancies taking bond distance into account, while Van Derveer *et al.* (1993) assumed ideally ordered octahedral sites and ordered tetrahedral sites, except for the two B-sites. This is an over simplification, as there is actually considerable disorder in all sites. In the three structure determinations, there is consensus for the location of the B at T1 and T4, with T1 having Si half occupied and T4 almost entirely occupied by B. Aluminum at the tetrahedral sites is always in partial occupation with Si; at octahedral sites Al is partially substituted by Mg, while Mg is well ordered at its own sites. Ordering in the serendibite structure, as reported by Van Derveer *et al.* (1993), is oversimplified.

Grew (2002) has compiled a review of the borosilicate minerals that includes the degree of ordering within the structure of each mineral species in addition to the occurrence(s) of each species. There is no clear evidence for ordering with respect to occurrence. The degree of ordering may be more dependent on the long-

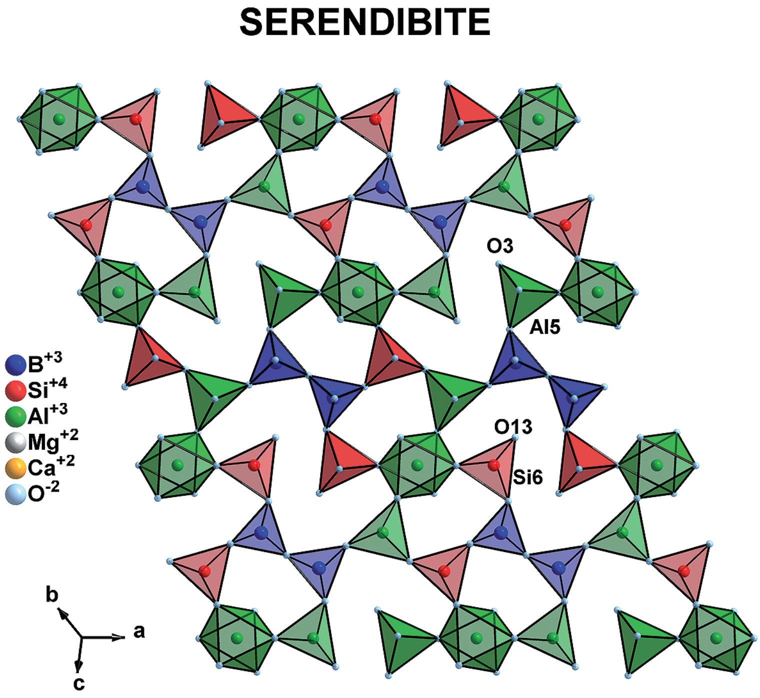

FIG. 4. Serendibite 'tetrahedral' layer consisting of tetrahedral chains cross-linked by Al in octahedral coordination.

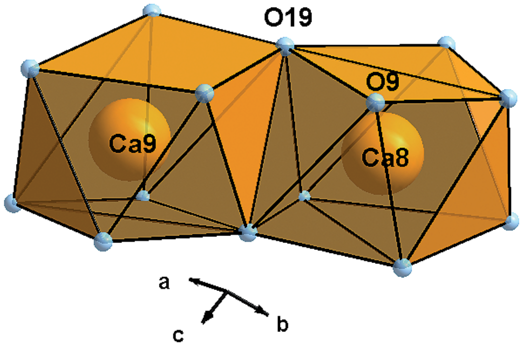

FIG. 5. Edge sharing Ca-centered, square antiprism, polyhedra.

term stability of an environment of formation than on the actual conditions of formation. In contrast to borosilicate minerals, beryllosilicate minerals are well ordered (Grice 2010) because they occur in stable crystallization environments in granite and granitic pegmatites and in alkaline rocks and syenitic pegmatites.

The concept of the coordination sequence (CS) was first introduced by Brunner & Laves (1971) and was initially called 'growth series', which emphasizes its close relationship to the process of crystal growth. The CS is a number sequence that tallies atoms bonded in each subsequent shell of a defined diameter. In this study we chose cations that are coordinated to next-nearest cation neighbors. For sites to be considered as part of the same CS, they must share a common O atom. These sites are in consecutive spheres of approximately 3.2 Å. Topological density (TD) is the summation of nodes for a defined series of shells of coordination sequence. The topological density summed over six shells is given in Table 7. Some generalizations may be made: the Ca sites have the lowest TD (~ 250) despite the fact that they have the highest coordination number. The cations in the octahedral band have the highest TD (~ 400). Of the six tetrahedral cations, four have a moderate TD ~ 350. These four tetrahedra all have four corners shared, while the two others, with TD ~ 250, only have three shared corners, *i.e.*, an interrupted net.

No doubt the dissolution of serendibite is dependent on these TD values. The voids in the structure (Figs. 4 and 6) are adjacent to the sites of lowest TD, *i.e.*, the Ca sites in the octahedral plane and Al5 and Si6 in the

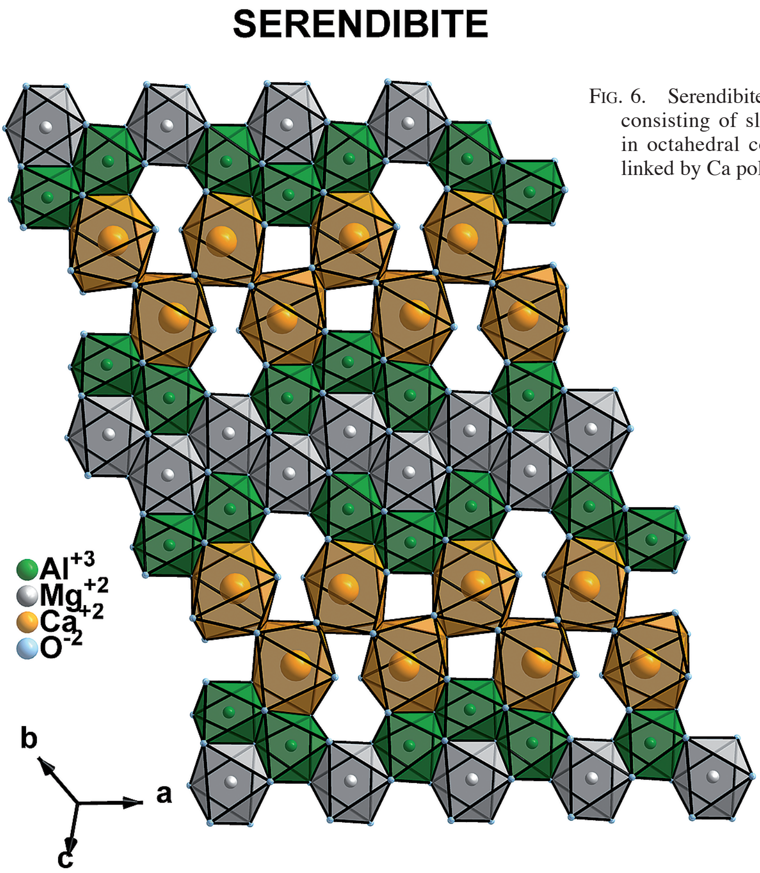

FIG. 6. Serendibite 'octahedral' layer consisting of slabs of Al and Mg in octahedral coordination cross-linked by Ca polyhedral chains.

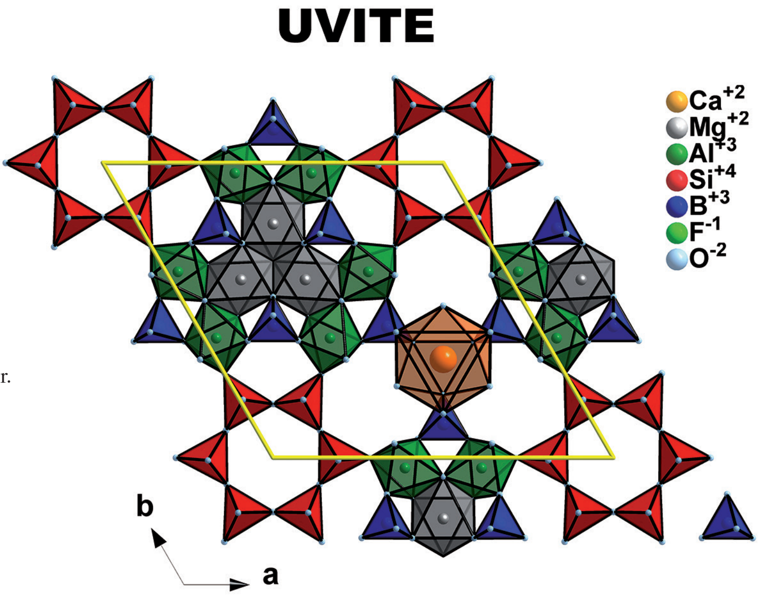

FIG. 7. Uvite layer.

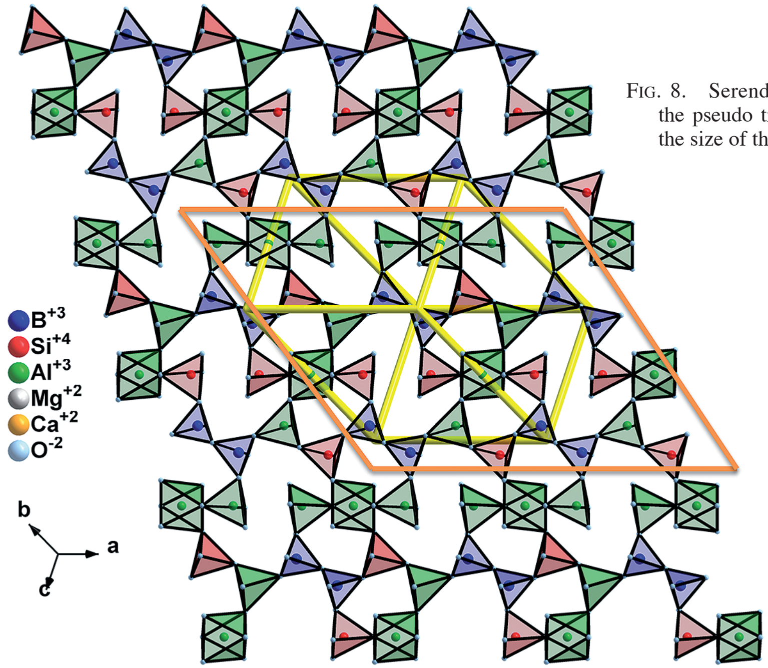

FIG. 8. Serendibite, unit cell in yellow indicating the pseudo trigonal [111] axis. The orange net is the size of the uvite cell, 15 × 15 Å with γ ~ 120°.

TABLE 7. SERENDIBITE SITE ASSIGNMENTS

Site	*apfu* assignment[1]	*epfu*[2]	e calc[3]	BVS[4]	VS[5]	TD[6]	B & V[7]	Van D *et al.*[8]	O site	BVS[3]	O Co-ord
Ca8	Ca0.95Na0.05	19.56	19.55	2.19	1.95	250	Ca0.82Mg0.10	Ca0.78Na0.22	O1	1.99	IV
Ca9	Ca0.95Na0.05	20.00	19.55	2.18	1.95	244	Ca0.82Mg0.11	Ca0.82Na0.18	O2	1.97	IV
Mg5	Mg1.00	12.00	12.00	1.95	2.00	371	Mg0.96Fe0.04	Mg1.0	O3	1.69	III
Mg6	Mg0.849Al0.151	12.47	12.15	2.13	2.15	396	Mg0.97Fe0.03	Mg1.0	O4	1.72	IV
Al1	Al0.935Mg0.065	13.01	12.95	2.69	2.94	406	Al0.95Fe0.05	Al1.0	O5	1.87	IV
Al2	Al0.843Mg0.157	13.10	12.84	2.62	2.84	402	Al0.95Fe0.05	Al1.0	O6	2.01	IV
Al3	Al0.714Mg0.286	13.00	12.71	2.54	2.71	381	Al0.65Mg0.25Fe0.10	Al1.0	O7	2.09	III
Al4	Al0.643Mg0.357	12.83	12.64	2.47	2.64	398	Al0.75Mg0.25	Al1.0	O8	1.97	IV
Al7	Al0.870Mg0.130	13.00	12.87	2.58	2.87	388	Al0.95Fe0.05	Al1.0	O9	2.04	IV
Σoct	Al3.267Mg2.733	89.41	88.16				Al4.25Mg2.43Fe0.32	Al5.0Mg2.0	O10	2.14	IV
									O11	1.98	IV
B1	B0.619Si0.381	7.36	8.43	3.37	3.38	330	B0.66Al0.34	B0.65Si0.35	O12	1.95	IV
Si2	Si0.840Al0.160	13.69	13.84	3.66	3.84	351	Si1.0	Si1.0	O13	1.77	III
$Al3^{IV}$	Al0.738Si0.262	13.54	13.26	2.97	3.26	365	Al0.75Si0.25	Al1.0	O14	1.73	IV
B4	B0.975Si0.025	5.35	5.26	2.99	3.02	336	B1.0	B0.98Si0.02	O15	1.88	IV
$Al5^{IV}$	Al0.508Si0.492	13.70	13.49	3.22	3.49	265	Si0.75Al0.25	Si1.0	O16	1.89	IV
Si6	Si0.831Al0.169	13.85	13.83	3.64	3.83	243	Si1.0	Si1.0	O17	2.07	III
Σtet	Si2.831B1.594Al1.571	67.49	68.11				Si3.00B1.66Al1.34	Si3.37B1.63Al1.00	O18	1.93	IV
									O19	2.10	IV
									O20	2.04	IV

[1] Atoms per formula unit
[2] *epfu* electrons per formula unit is derived from refined scattering power
[3] e⁻ calc is the electron sum for the site assignment
[4] Bond valence sum (Brese & O'Keeffe 1991)
[5] Valence sum of site assignment
[6] Topological density summation to six population clusters or shells
[7] Buerger & Ventkatakrishnan (1974): $(Ca_{1.64}Mg_{0.21})_{\Sigma1.85}$ $(Al_{4.25}Mg_{2.43}Fe_{0.32})_{\Sigma6}$ $(Si_{3.00}B_{1.66}Al_{1.34})_{\Sigma6}O_{20}$
[8] Van Derveer *et al.* (1993): $(Ca_{1.60}Na_{0.40})_{\Sigma2}$ $(Al_{5.00}Mg_{2.00})_{\Sigma6}$ $(Si_{3.37}B_{1.63}Al_{1.00})_{\Sigma6}O_{20}$
Present study: $(Ca_{1.90}Na_{0.10})_{\Sigma2}$ $(Al_{3.27}Mg_{2.73})_{\Sigma6}$ $(Si_{2.83}B_{1.60}Al_{1.57})_{\Sigma6}O_{20}$

tetrahedral plane. These weaknesses in the structural bonding would be active dissolution sites (Fig 1). The cation units with the highest TD's would tend to be the most stable.

In the uvite structure layering of polyhedra can be determined, but unlike serendibite, there is only one layer type (Fig. 7) stacked three times in the rhombohedral cell. In the case of pseudomorphism of serendibite by uvite, serendibite has a pseudo-trigonal cell that matches the footprint (cell dimensions and rhombohedral net) of uvite. In Figure 8 the pseudo-three-fold axis parallels [111] of serendibite and the 15 × 15 Å trigonal net ($\gamma \sim 120°$) of uvite overlays perfectly in serendibite (Fig. 8). The alteration of serendibite to uvite would necessitate some degree of mass transfer, *i.e.*, a decrease in Ca and Al and an increase in B and Si (seen in the pseudomorphs as scattered grains of calcite and spinel). The refit of modular units in a hydrothermal system from serendibite to uvite would involve transitioning the S-voids into six-membered rings, ordering the B tetrahedra into B triangular coordination, regrouping of octahedral plates, and flushing some of the [CaO_8] polyhedra.

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