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STRONTIOGINORITE: CRYSTAL-STRUCTURE ANALYSIS AND HYDROGEN BONDING

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Abstract

Strontioginorite, ideally $SrCaB_{14}O_{20}(OH)_6•5H_2O$, from the Potash Corporation of Saskatchewan (New Brunswick Division) mine at Penobsquis, Kings County, New Brunswick, occurs in the Upper Halite member of the Windsor Group evaporites, and is associated with halite, sylvite, hilgardite, volkovskite and trembathite. Electron-microprobe analysis, supported by a single-crystal analysis of its structure, yield: CaO 7.47 (6.66–8.10), SrO 12.23 (11.30–13.69), (B_2O_3) 61.22 and (H_2O) 18.10, for a total of 99.02 wt.%. The empirical formula, based on 31 anions, is $Ca_{0.94}Sr_{1.06}B_{14}O_{20}(OH)_6•5H_2O$. Strontioginorite is monoclinic, $P2_1/a$, with refined unit-cell parameters a 12.8171(4), b 14.4576(4), c 12.8008(4) Å, β 101.327(1)°, V 2325.8(2) Å^3, $Z = 4$. The crystal structure refined to an R index of 0.024 for 6,784 unique, observed (>4σ F_o) reflections. The (010) sheets of borate polyhedra are weakly cross-linked by Sr and Ca polyhedra. The H_2O and OH groups strengthen the cross-linkage with hydrogen bonding. The fundamental building block (FBB) within the structure, 8Δ6□:[φ]<Δ2□>|<Δ2□>|<Δ2□>|–[φ]<Δ2□>|<Δ2□>|<Δ2□>|–2Δ, is compared to that in the structure of other complex borates, such as nobleite and strontioborite.

Keywords: strontioginorite, crystal structure, borate, polymerization, evaporite, hydrogen bonding.

Sommaire

La strontioginorite, de composition idéale $SrCaB_{14}O_{20}(OH)_6•5H_2O$, est signalée dans la mine de la société Potash Corporation of Saskatchewan (New Brunswick Division) à Penobsquis, comté de Kings, au Nouveau-Brunswick, dans le membre désigné Upper Halite des évaporites du groupe de Windsor, en association avec halite, sylvite, hilgardite, volkovskite et trembathite. Les analyses effectuées avec une microsonde électronique, étayées par les résultats de l'ébauche de la structure déterminée sur monocristal, ont donné: CaO 7.47 (6.66–8.10), SrO 12.23 (11.30–13.69), (B_2O_3) 61.22 and (H_2O) 18.10, pour un total de 99.02% (poids). La formule empirique, fondée sur 31 anions, est $Ca_{0.94}Sr_{1.06}B_{14}O_{20}(OH)_6•5H_2O$. La strontioginorite est monoclinique, $P2_1/a$, et possède les paramètres réticulaires a 12.8171(4), b 14.4576(4), c 12.8008(4) Å, β 101.327(1)°, V 2325.8(2) Å^3, Z = 4. La structure a été affinée jusqu'à un résidu R de 0.024 pour 6,784 réflexions uniques observées (>4σ F_o). Les feuillets (010) de polyèdres de borate sont faiblement liés transversalement par des polyèdres contenant Sr et Ca. Les groupes de H_2O et OH renforcent les liens entre feuillets avec des liaisons hydrogène. Le bloc structural fondamental de cette structure, 8Δ6□:[φ]<Δ2□>|<Δ2□>|<Δ2□>|–[φ]<Δ2□>|<Δ2□>|<Δ2□>|–2Δ, est comparé à celui dans la structure d'autres borates complexes, tels la nobléite et la strontioborite.

(Traduit par la Rédaction)

Mots-clés: strontioginorite, structure cristalline, borate, polymérisation, évaporite, liaisons hydrogène.

Introduction

Strontioginorite, ideally $SrCaB_{14}O_{20}(OH)_6•5H_2O$, from the Potash Corporation of Saskatchewan (New Brunswick Division) mine at Penobsquis, Kings County, New Brunswick occurs in the Upper Halite member of the Windsor Group evaporites, associated with halite, sylvite, hilgardite, volkovskite, trembathite, commonly with the silicoborates danburite and howlite, and rarely with veatchite and hydroboracite (Grice *et al*. 2005). The evaporites are Mississippian in age and occur in the Moncton sub-basin, part of the Fundy geosyncline, a northeasterly trending depositional trough extending through southern New Brunswick, Nova Scotia and western Newfoundland (Waugh & Urquhart 1983, Webb & Roulston 1994). Strontioginorite forms late in the crystallization sequence of the borate minerals. Prismatic crystals are clear, colorless and elongate on [001]. These crystals afforded excellent material for a crystal-structure refinement. Konnert *et al*. (1970) refined the structure of strontioginorite using a crystal of type material from Reyerhausen, Germany.

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They were able to refine the structure to an *R* index of 0.064, but were unable to determine the position of the hydrogen atoms.

The presence of borate minerals within two potash mines in the Penobsquis–Sussex area of New Brunswick was first noted in the early 1980s in residue from the drilling operations; the minerals were subsequently identified in the laboratories of the mining companies and at various institutions (Roulston & Waugh 1981). The list of borate minerals compiled from those earlier investigations and from the present study includes boracite, brianroulstonite, colemanite, congolite, danburite, ginorite, hilgardite-1*A*, hilgardite-4*M*, howlite, hydroboracite, inyoite, penobsquisite, priceite, pringleite, ruitenbergite, strontioginorite, szaibélyite, trembathite, tyretskite, veatchite, volkovskite and walkerite.

Chemical Composition

Electron-microprobe analysis

The chemical analyses were performed on a JEOL 733 electron microprobe in wavelength-dispersion (WD) mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (C. Davidson, CSIRO, pers. commun.). The operating voltage was 15 kV, and the beam current was 20 nA. The beam diameter varied from 20 to 40 μm. The following standards were used: danburite (Ca*K*α), and celestine (Sr*L*α). Several 100-s energy-dispersion (ED) scans were made, and indicated no elements with Z > 8 other than those reported here. Magnesium, Mn, Fe and Cl were sought but not detected. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. Nine electron-microprobe analyses were performed on different grains. The presence of H_2O was confirmed by crystal-structure analysis.

The chemical composition is: CaO 7.47 (6.66–8.10), SrO 12.23 (11.30–13.69), (B_2O_3) 61.22 and (H_2O) 18.10, for a total of 99.02 wt.%. The empirical formula based on 31 anions is $Ca_{0.94}Sr_{1.06}B_{14}O_{20}(OH)_6{\bullet}5H_2O$.

Crystal-Structure Determination

The single crystal of strontioginorite used for the collection of X-ray intensity data measured 0.30 × 0.10 × 0.06 mm. Intensity data were collected on a fully automated Siemens *P*4 four-circle diffractometer equipped with an APEX 4K CCD detector and operated at 50 kV, 40 mA, with graphite-monochromated Mo*K*α radiation. A full sphere of intensity data was collected up to 2θ = 60° using 30 s frames at frame widths of 0.15°. 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 1. The three-dimensional data were reduced for Lorentz, polarization, and background effects, and multiply-measured reflections were averaged using the Bruker program SAINT. An empirical absorption-correction was applied (SADABS, Sheldrick 1998), which reduced the internal residual for merging data in 2/*m* from 3.4% before the absorption correction to 2.2% after the absorption correction.

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 0.926, which suggests the centrosymmetric space-group $P2_1/a$. The initial coordinates assigned to the atoms were those of Konnert *et al.* (1970), except for the hydrogen atoms, which were located on difference-Fourier maps in subsequent refinements. The site occupancies of Ca and Sr were allowed to refine, and their final values were 0.92(1) and 1.016(2) atoms per formula unit (*apfu*), respectively. The total *epfu* from the electron-microprobe analysis, 57.4, agrees within 3.5% of that determined from crystal-structure analysis. Positions of the H atoms were refined with fixed isotropic displacement factors, as refined values were unrealistic, but without constraints on the O–H distances. The addition of an isotropic extinction-correction did not improve the refinement, nor was there any evidence of twinning. The maximum and minimum electron-densities in the final cycle of refinement were +0.63 and –0.39 $e^-/Å^3$. The final positional and anisotropic displacement parameters are given in Table 2, selected bond-lengths and angles, in Table 3, and hydrogen-bonding scheme, in Table 4. Tables listing the observed and calculated structure-factors as well as the anisotropic displacement-parameters may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. STRONTIOGINORITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Simplified formula: $SrCaB_{14}O_{20}(OH)_6{\bullet}5H_2O$

Space group: $P2_1/a$	Reflections collected: 27,132
Radiation: Mo*K*α	Unique reflections: 6,784
Graphite monochromator	Observed reflections (> 4σF_o): 6,282
a 12.8171(4) Å	*R*(int) = 0.0177
b 14.4576(4) Å	$\|E^2 - 1\|$ = 0.926
c 12.8008(4) Å	Goof = 0.978 (all data)
β 101.327(1)°	$R = \Sigma(\|F_o\| - \|F_c\|) / \Sigma\|F_o\|$ = 0.024 (for F_o), and 0.026 (for all *F*)
V 2325.8(2) Å^3	
Z = 4	
μ = 2.67 mm^{-1}	$wR^2 = [\Sigma w (F_o - F_c)^2 / \Sigma w (F_o)^2] = 0.0662$
Crystal size 0.30 × 0.10 × 0.06 mm	$w = 1/\{\sigma^2 F_o^2 + [0.1(\text{Max}(F_o^2,0) + 2F_c^2)/3]^2\}$

TABLE 2. STRONTIOGINORITE: ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2)

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Sr	0.61773(1)	0.17104(1)	0.73631(1)	0.01255(7)	0.01385(8)	0.01270(7)	0.00090(4)	0.00518(5)	0.00081(4)	0.01266(5)
Ca	0.12691(2)	0.21922(2)	0.24657(2)	0.0116(1)	0.0145(1)	0.012(1)	-0.00020(8)	0.00323(9)	0.00047(8)	0.01271(9)
B1	0.3906(1)	0.2019(1)	-0.1234(1)	0.0103(6)	0.0156(6)	0.0097(6)	-0.0020(5)	0.0034(4)	-0.0007(5)	0.0116(2)
B2	0.4329(1)	0.3028(1)	0.0508(1)	0.0108(6)	0.0158(6)	0.0106(6)	-0.0014(5)	0.0033(5)	-0.0015(5)	0.0122(2)
B3	0.2632(1)	0.1964(1)	0.0125(1)	0.0099(6)	0.0156(6)	0.0102(6)	-0.0016(5)	0.0034(4)	-0.0011(5)	0.012(2)
B4	0.5752(1)	0.2547(1)	-0.0426(1)	0.0113(6)	0.0177(7)	0.0116(6)	-0.0001(5)	0.0028(5)	-0.0002(5)	0.0134(3)
B5	0.3425(1)	0.2579(1)	0.1940(1)	0.0117(6)	0.0161(6)	0.0110(6)	-0.0004(5)	0.0030(5)	0.0007(5)	0.0128(3)
B6	0.3041(1)	0.0563(1)	-0.0793(1)	0.0180(7)	0.0169(7)	0.0196(7)	-0.0030(6)	0.0080(6)	-0.0018(5)	0.0176(3)
B7	0.3909(1)	0.3198(1)	0.3790(1)	0.0103(6)	0.0136(6)	0.0092(6)	0.0003(5)	0.0027(4)	0.0005(5)	0.0110(2)
B8	0.4231(1)	0.2027(1)	0.5392(1)	0.0108(6)	0.0127(6)	0.0107(6)	-0.0002(5)	0.0035(4)	0.0000(5)	0.0112(2)
B9	0.2553(1)	0.3107(1)	0.5049(1)	0.0091(6)	0.0134(6)	0.0106(6)	-0.0002(5)	0.0032(4)	0.0004(5)	0.0108(2)
B10	0.5702(1)	0.2545(1)	0.4567(1)	0.0100(6)	0.0128(6)	0.0114(6)	-0.0013(5)	0.0024(4)	-0.0002(5)	0.0113(2)
B11	0.3357(1)	0.2527(1)	0.6870(1)	0.0100(6)	0.0142(6)	0.0108(6)	-0.0006(5)	0.0027(4)	-0.0013(5)	0.0116(2)
B12	0.2918(1)	0.4570(1)	0.4154(1)	0.0162(6)	0.0146(7)	0.0168(6)	0.0019(5)	0.0063(5)	0.0013(5)	0.0154(3)
B13	0.4098(1)	0.0662(1)	0.4099(1)	0.0162(6)	0.0130(6)	0.0148(6)	-0.0007(5)	0.0054(5)	0.0006(5)	0.0143(3)
B14	0.5245(1)	0.0623(1)	0.2736(1)	0.0171(6)	0.0148(7)	0.0172(6)	-0.0011(5)	0.0068(5)	0.0004(5)	0.0159(3)
O1	0.36670(7)	0.23073(6)	-0.01619(7)	0.0094(4)	0.0149(4)	0.0096(4)	-0.0021(3)	0.0031(3)	-0.0016(3)	0.0112(2)
O2	0.43256(8)	0.28843(8)	0.16350(7)	0.0130(4)	0.0273(5)	0.0098(4)	-0.0028(4)	0.0037(3)	-0.0054(4)	0.0165(2)
O3	0.26259(8)	0.21563(8)	0.12386(7)	0.0128(4)	0.0258(5)	0.0102(4)	-0.0036(4)	0.0044(3)	-0.0040(4)	0.0150(2)
O4	0.25822(8)	0.09641(7)	-0.00390(8)	0.0224(5)	0.0153(5)	0.0228(5)	-0.0040(4)	0.0134(4)	-0.0039(4)	0.0189(2)
O5	0.36394(8)	0.10376(7)	-0.13751(8)	0.0211(5)	0.0150(5)	0.0176(4)	-0.0038(4)	0.0106(4)	-0.0033(4)	0.0170(2)
O6	0.50382(7)	0.21244(7)	-0.12115(7)	0.0096(4)	0.0231(5)	0.0125(4)	-0.0036(4)	0.0034(3)	-0.0018(4)	0.0149(2)
O7	0.54432(7)	0.29426(7)	0.04367(7)	0.0105(4)	0.0266(5)	0.0150(4)	-0.0070(4)	0.0050(3)	-0.0032(4)	0.0170(2)
OH8	0.2939(1)	-0.03712(8)	-0.1001(1)	0.0475(8)	0.0165(5)	0.0433(7)	-0.0097(5)	0.0331(6)	-0.0104(5)	0.0324(3)
OH9	0.38786(9)	0.39242(7)	0.01462(9)	0.0253(5)	0.0149(5)	0.0249(5)	-0.0012(4)	-0.0014(4)	0.0014(4)	0.0226(2)
O10	0.17728(7)	0.24475(8)	-0.05638(7)	0.0098(4)	0.0282(5)	0.0138(4)	0.0043(4)	0.0036(3)	0.0014(4)	0.0171(2)
O11	0.32221(7)	0.26825(7)	0.29316(7)	0.0111(4)	0.0217(5)	0.0097(4)	-0.0025(3)	0.0030(3)	-0.0021(4)	0.0140(2)
O12	0.36268(7)	0.28403(6)	0.48183(7)	0.0085(4)	0.0131(4)	0.0096(4)	0.0011(3)	0.0032(3)	0.0010(3)	0.0102(2)
O13	0.41210(7)	0.20398(7)	0.65046(7)	0.0138(4)	0.0155(4)	0.0104(4)	0.0013(3)	0.0050(3)	0.0024(3)	0.0129(2)
O14	0.25872(7)	0.30099(7)	0.61876(7)	0.0118(4)	0.0201(5)	0.0096(4)	0.0012(3)	0.0034(3)	0.0029(4)	0.0136(2)
O15	0.23477(7)	0.40711(76	0.47531(7)	0.0141(4)	0.0130(4)	0.0179(4)	0.0017(3)	0.0074(3)	0.0022(3)	0.0144(2)
O16	0.36793(8)	0.41761(7)	0.36912(8)	0.0170(4)	0.0138(4)	0.0182(4)	0.0033(4)	0.0084(4)	0.0033(4)	0.0157(2)
O17	0.50387(7)	0.30540(7)	0.38105(7)	0.0090(4)	0.0165(4)	0.0120(4)	0.0019(3)	0.0030(3)	0.0007(3)	0.0124(2)
O18	0.53563(7)	0.21339(7)	0.53912(7)	0.0098(4)	0.0165(4)	0.0124(4)	0.0024(3)	0.0038(3)	0.0010(3)	0.0127(2)
OH19	0.2709(1)	0.5492(8)	0.3968(1)	0.0353(6)	0.0153(5)	0.0426(7)	0.0092(5)	0.0265(6)	0.0088(5)	0.0285(3)
O20	0.38137(8)	0.11539(7)	0.49021(8)	0.0161(4)	0.0139(4)	0.0165(4)	-0.0028(4)	0.0074(4)	-0.0021(4)	0.0149(2)
OH21	0.37338(9)	-0.02187(7)	0.38927(8)	0.0314(6)	0.0154(5)	0.0231(5)	-0.0053(4)	0.0165(4)	-0.0072(4)	0.0218(2)
O22	0.47503(8)	0.10394(7)	0.34641(8)	0.0254(5)	0.0137(5)	0.0226(5)	-0.0036(4)	0.0152(4)	-0.0034(4)	0.0192(2)
OH23	0.5035(1)	-0.02604(8)	0.2416(1)	0.0324(6)	0.0156(5)	0.0407(6)	-0.0095(5)	0.0260(5)	-0.0065(4)	0.0270(3)
OH24	0.59516(9)	0.11733(8)	0.23334(9)	0.0278(5)	0.0168(5)	0.0264(5)	-0.0045(4)	0.0179(4)	-0.0056(4)	0.0220(2)
O25	0.17299(7)	0.25171(7)	0.44172(7)	0.0093(4)	0.0169(4)	0.0133(4)	-0.0022(3)	0.0035(3)	-0.0014(3)	0.0130(2)
O26	0.32821(8)	0.25721(7)	0.79196(7)	0.0141(4)	0.0218(5)	0.0095(4)	0.0008(4)	0.0037(3)	0.0035(4)	0.0149(2)
OW27	0.1091(1)	0.1503(1)	0.7210(1)	0.0364(7)	0.0248(6)	0.0320(6)	-0.0023(5)	0.0110(5)	0.0029(5)	0.0305(3)
OW28	0.1546(1)	0.0621(1)	0.2712(1)	0.0446(8)	0.0242(6)	0.0431(7)	0.0065(6)	0.0218(6)	0.0096(6)	0.0355(3)
OW29	0.2366(1)	0.45021(9)	0.84915(9)	0.0282(6)	0.0267(6)	0.0231(5)	-0.0003(4)	0.0009(4)	0.0037(5)	0.0266(2)
OW30	0.0184(1)	0.0384(1)	0.8665(1)	0.0398(7)	0.0318(7)	0.0341(7)	0.0007(6)	0.0075(6)	0.0028(6)	0.0352(3)
OW31	0.0519(1)	-0.0244(1)	0.4009(1)	0.0318(7)	0.0352(7)	0.0432(7)	0.0071(6)	0.0107(6)	0.0090(6)	0.0363(3)
H8	0.256(2)	-0.059(2)	-0.071(2)	0.05						
H9	0.415(2)	0.432(1)	0.056(2)	0.05						
H19	0.230(2)	0.565(2)	0.430(2)	0.05						
H21	0.338(2)	-0.038(2)	0.432(2)	0.05						
H23	0.551(1)	-0.045(2)	0.208(2)	0.05						
H24	0.619(2)	0.090(2)	0.198(2)	0.05						
H27A	0.088(2)	0.148(2)	0.685(2)	0.05						
H27B	0.123(2)	0.136(2)	0.774(2)	0.05						
H28A	0.135(2)	0.037(2)	0.319(2)	0.05						
H28B	0.208(10)	0.024(9)	0.262(10)	0.05						
H29A	0.284(2)	0.422(2)	0.897(2)	0.05						
H29B	0.218(2)	0.494(1)	0.883(2)	0.05						
H30A	-0.030(2)	0.012(2)	0.815(2)	0.05						
H30B	-0.025(2)	0.065(2)	0.908(2)	0.05						
H31A	0.022(2)	-0.079(2)	0.381(2)	0.05						
H31B	-0.006(2)	0.015(2)	0.392(2)	0.05						

Description of the Structure

The crystal structure of strontioginorite is a complex (010) sheet structure. The Sr and Ca atoms are arranged in planes parallel to {010}, but do not link directly together. They are located within the sheet of borate polyhedra. These sheets are cross-linked by H-bonding and the intralayer bonds of the large Sr and Ca polyhedra (Fig. 1). As discussed in Konnert *et al*. (1970), the sheet structure is in accord with the (010) platy habit and perfect cleavage.

Sheet of borate polyhedra

The borate sheet structure consists of fourteen crystallographically distinct borate polyhedra, eight of which are triangular [(BO_3) groups] and six of which are tetrahedral [(BO_4) groups] (Fig. 2). There are three

TABLE 3. STRONTIOGINORITE: SELECTED BOND-LENGTHS (Å) AND BOND ANGLES (°)

Sr-OW29	2.572(1)	Ca-OW28	2.311(1)	B1-O26	1.454(2)	O26-O6	110.9(1)
Sr-OW27	2.590(1)	Ca-OH24	2.398(1)	B1-O6	1.454(2)	O26-O5	111.1(1)
Sr-O14	2.600(1)	Ca-O25	2.496(1)	B1-O5	1.462(2)	O26-O1	110.1(1)
Sr-O18	2.610(1)	Ca-O2	2.512(1)	B1-O1	1.521(2)	O6-O5	108.1(1)
Sr-O6	2.620(1)	Ca-O11	2.557(1)	<B1-O>	<1.473>	O6-O1	109.3(1)
Sr-OH23	2.657(1)	Ca-O3	2.563(1)			O5-O1	107.1(1)
Sr-O13	2.691(1)	Ca-O17	2.578(1)			<O-B-O>	<109.4>
Sr-OH21	2.706(1)	Ca-O7	2.612(1)				
Sr-O26	2.847(1)	<Ca-O>	<2.503>				
Sr-O10	2.883(1)						
<Sr-O>	<2.678>						
B2-O7	1.455(2)	O7-OH9	112.8(1)	B3-O10	1.448(2)	O10-O3	110.7(1)
B2-OH9	1.457(2)	O7-O2	104.1(1)	B3-O3	1.455(2)	O10-O4	112.6(1)
B2-O2	1.458(2)	O7-O1	110.9(1)	B3-O4	1.460(2)	O10-O1	106.8(1)
B2-O1	1.502(2)	O9-O2	111.4(1)	B3-O1	1.527(2)	O3-O4	108.8(1)
<B2-O>	<1.468>	O9-O1	106.9(1)	<B3-O>	<1.472>	O3-O1	110.2(1)
		O2-O1	110.8(1)			O4-O1	107.7(1)
		<O-B-O>	<109.5>			<O-B-O>	<109.5>
B4-O10	1.354(2)	O10-O6	115.5(1)	B5-O11	1.354(1)	O11-O2	124.2(1)
B4-O6	1.362(2)	O10-O7	122.9(1)	B5-O2	1.362(1)	O11-O3	114.1(1)
B4-O7	1.366(2)	O6-O7	121.6(1)	B5-O3	1.366(1)	O2-O1	121.7(1)
<B4-O>	<1.361>	<O-B-O>	<120.0>	<B5-O>	<1.361>	<O-B-O>	<120.0>
B6-O4	1.355(2)	O4-O5	123.1(1)	B7-O16	1.445(2)	O16-O17	109.0(`)
B6-O5	1.356(2)	O4-OH8	121.2(1)	B7-O17	1.458(2)	O16-O11	110.4(1)
B6-OH8	1.378(2)	O5-OH8	115.6(1)	B7-O11	1.469(2)	O16-O12	109.2(1)
<B6-O>	<1.361>	<O-B-O>	<120.0>	B7-O12	1.522(2)	O17-O11	112.8(1)
				<B7-O>	<1.474>	O17-O12	109.9(1)
						O11-O12	105.4(1)
						<O-B-O>	<109.4>
B8-O18	1.451(2)	O8-O13	106.6(1)	B9-O15	1.455(2)	O15-O14	108.8(1)
B8-O13	1.459(2)	O8-O20	111.8(1)	B9-O14	1.456(2)	O15-O25	109.8(1)
B8-O20	1.463(2)	O8-O12	109.3(1)	B9-O25	1.470(2)	O15-O25	108.5(1)
B8-O12	1.516(2)	O13-O20	109.4(1)	B9-O12	1.514(2)	O14-O25	111.9(1)
<B8-O>	<1.472>	O13-O12	109.0(1)	<B9-O>	<1.474>	O14-O12	108.7(1)
		O20-O12	110.7(1)			O25-O12	109.0(0)
		<O-B-O>	<109.5>			<O-B-O>	<109.4>
B10-O18	1.359(2)	O18-017	122.2(1)	B11-O13	1.362(2)	O13-O26	123.8(1)
B10-O17	1.370(2)	O18-O25	123.2(1)	B11-O26	1.367(2)	O13-O14	121.3(1)
B10-O25	1.371(2)	O17-O25	114.6(1)	B11-O14	1.374(2)	O26-O14	114.9(1)
<B10-O>	<1.367>	<O-B-O>	<120.0>	<B11-O>	<1.368>	<O-B-O>	<120.0>
B12-O16	1.362(2)	O16-O15	122.1(1)	B13-O20	1.358(2)	O20-OH21	120.2(1)
B12-O15	1.365(2)	O16-OH19	117.6(1)	B13-OH21	1.364(2)	O20-O22	121.3(1)
B12-OH19	1.370(2)	O15-OH19	120.3(1)	B13-O22	1.387(2)	OH21-O22	118.5(1)
<B12-O>	<1.366>	<O-B-O>	<120.0>	<B13-O>	<1.370>	<O-B-O>	<120.0>
B14-OH23	1.352(2)	OH23-O22	122.1(1)				
B14-O22	1.366(2)	OH23-OH24	122.6(1)				
B14-OH24	1.380(2)	O22-OH24	115.3(1)				
<B14-O>	<1.366>	<O-B-O>	<120.0>				

types of triangular coordination, the common [BO_3], the rarer [$BO_2(OH)$] and the very rare [$BO(OH)_2$]. There are two types of tetrahedral coordination, [BO_4] and [$BO_3(OH)$] (Table 3). Those O atoms bonded to two or three B atoms are O^{2-} anions, whereas O atoms bonded to one B atom are part of an OH^- group. There are no H_2O groups bonded to B. The fundamental building block (FBB) given by Grice *et al*. (1999) is: 8Δ6□:[ϕ]<Δ2□>|<Δ2□>|<Δ2□>|–[ϕ]<Δ2□>|<Δ2□>|<Δ2□>|–2Δ. This sequence of symbols (Burns *et al*. 1995) denotes three rings, shown in <brackets>, each consisting of one triangular polyhedron, Δ, and two tetrahedral polyhedra, □, *i.e.,* one ring is symbolized as <Δ2□>. Each set of three rings shares a common oxygen atom, denoted [ϕ]. In the FBB, there are two sets of these three-fold rings, the second of which is decorated by two additional triangular borate polyhedra. These decorations are the triangular [$BO_2(OH)$] and [$BO(OH)_2$] polyhedra.

Sr and Ca polyhedra

The Sr and Ca polyhedra may be considered as part of the sheets, as they fit within the borate polyanion and are coordinated primarily within a single sheet. Strontium is 10-coordinated to two H_2O groups, two OH groups and six oxygen atoms. The bond distances range from 2.572 to 2.883 Å, with an average bond-distance of 2.678 Å (Table 3). Of the 10 bonds, only one, Sr–OH23, actually cross-links adjacent sheets (Fig. 1). The remaining bonds are intralayer or link to a H_2O group. Calcium is 8-coordinated to one H_2O group, one OH group and six oxygen atoms. The bond distances range from 2.311 to 2.612 Å, with an average bond-distance of 2.503 Å (Table 3). Of the eight bonds, only one, Ca–OH24, actually cross-links adjacent sheets (Fig. 1). The remaining bonds are intralayer or link to a H_2O group.

TABLE 4. STRONTIOGINORITE: HYDROGEN BONDING

O_d, H	O_d-H (Å)	H-O_a (Å)	O_d-H-O_a (°)	O_d-O_a (Å)	O_a
OH8-H8	0.74(3)	2.22(3)	166(3)	2.944(2)	OH9
OH9-H9	0.81(3)	1.94(3)	170(3)	2.738(2)	OW30
OH19-H19	0.78(3)	2.04(3)	176(3)	2.816(2)	O20
OH21-H21	0.82(3)	1.82(3)	170(3)	2.632(2)	O15
OH23-H23	0.86(3)	1.76(3)	170(3)	2.611(2)	O5
OH24-H24	0.72(3)	1.98(3)	168(3)	2.689(2)	OH8
OW27-H27A	0.49(3)	none			
OW27-H27B	0.71(3)	none			
OW28-H28A	0.79(3)	1.86(3)	163(3)	2.629(2)	OW31
OW28-H28B	0.90(13)	2.02(12)	142(12)	2.790(2)	OW29
OW29-H29A	0.87(3)	1.85(3)	166(3)	2.707(2)	OH9
OW29-H29B	0.84(3)	2.11(3)	154(2)	2.889(2)	O4
OW30-H30A	0.89(3)	2.06(3)	166(2)	2.932(2)	OW28
OW30-H30B	0.92(3)	2.02(3)	171(2)	2.939(2)	OH9
OW31-H31A	0.89(3)	2.17(3)	146(2)	2.956(2)	OW27
OW31-H31B	0.93(3)	1.86(3)	174(2)	2.781(2)	O16

O_d: oxygen with H-bond donor; O_a: oxygen as H-bond acceptor.

H_2O and OH groups and hydrogen bonding

In strontioginorite, there are five H_2O groups; two groups are bonded to Sr, one group is bonded to Ca, and the remaining two H_2O groups are H-bonded to other H_2O groups or OH groups. The crystal-structure refinement indicates that all H_2O groups are fully occupied, even those that are only hydrogen-bonded within the structure. The full site-occupancy likely reflects the fact that the H_2O groups are critical to the cross-linkage of the Sr–Ca borate layers, thus contributing to the structural stability of the mineral. Figure 3 shows the hydrogen-bonding relationships for the H_2O groups, and Table 4 gives the appropriate bond-lengths for both the H-bond donor and H-bond acceptor. The two H_2O groups that are bonded by H-bonds only, OW30 and OW31, each have two H-donor bonds and one H-acceptor bond. The oxygen atom OW30 is a H-donor to OW28 and OH9 and a H-acceptor from H9. The oxygen atom OW31 is a H-donor for OW27 and O16, and a H-acceptor from H28A. The two H_2O groups bonded to Sr, OW27 and OW29, differ in their hydrogen bonds; OW27 is not a H-donor but is a H-acceptor from H31A, and OW29 is a H-donor to OH9 and O4 and a H-acceptor from OW31. The one H_2O group bonded to Ca, OW28, has three hydrogen bonds; OW28 is a H-donor to OW31 and OW29 and a H-acceptor from H30A.

All six OH groups are involved in H-bonding and all form polyhedron terminations that are not shared with another boron atom. Of the six groups, five are terminations to triangular polyhedra of boron, whereas the sixth, OH9, is a termination to a tetrahedral polyhedron of boron. The OH9 oxygen is a H-donor to OW30 and an H-acceptor from two other H_2O groups, OW29 and OW30. The hydroxyl groups OH8 and OH19 are both H-donors and H-acceptors, whereas the OH21, OH23 and OH24 hydroxyl groups are H-donors only. The rather unique scheme of bonding of these latter three OH groups can be attributed to their role in terminating borate polyhedra that are the "decorations" to the borate FBB (Fig. 4). In this scheme, OH21 is bonded to B13, whereas OH23 and OH24 are bonded to B14.

Discussion

The FBB for strontioginorite is 8Δ6□:[ϕ]<Δ2□>|<Δ2□>|<Δ2□>|–[ϕ]<Δ2□>|<Δ2□>|<Δ2□>|–2Δ. This FBB has a sub-unit with a finite cluster of 3Δ3□:[ϕ]<Δ2□>|<Δ2□>|<Δ2□>| consisting of three <Δ2□> rings that link to a common central oxygen atom through their tetrahedrally coordinated B atoms. This unit appears in many borate structures (1) as a finite

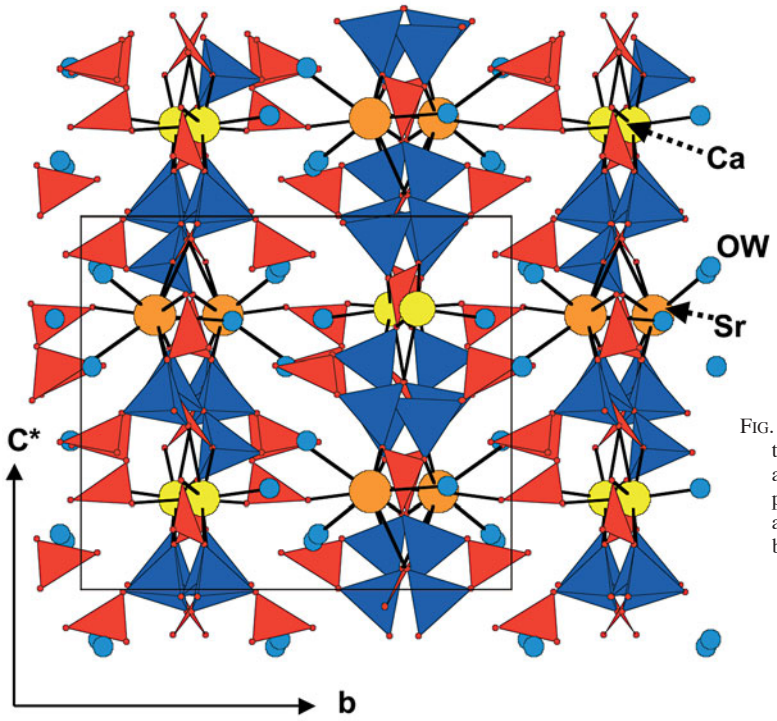

FIG. 1. Strontioginorite: [100] projection showing borate sheets of triangular (red) and tetrahedral (blue) polyhedra; Sr atoms (orange), Ca atoms (yellow) and H_2O groups (light blue) cross-link the borate sheets.

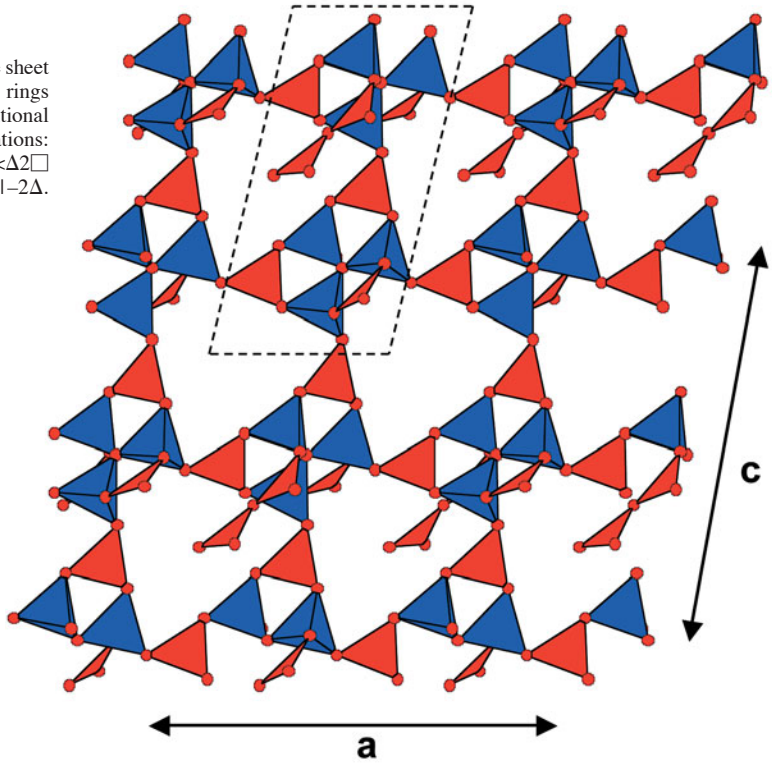

FIG. 2. Strontioginorite: (010) borate sheet consisting of six three-membered rings of borate polyhedra with an additional two triangular polyhedra as decorations: FBB 8Δ6□:[ϕ]<Δ2□>1<Δ2□>1<Δ2□>1–[ϕ]<Δ2□>1<Δ2□>1<Δ2□>1–2Δ. The FBB is outlined.

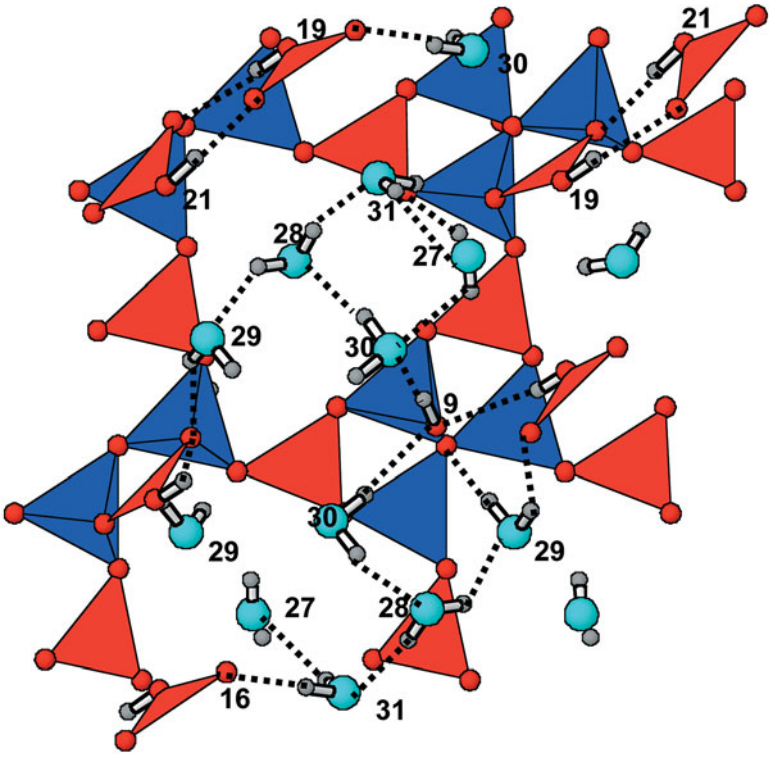

FIG. 3. Strontioginorite: [010] projection showing H-bonding scheme within the H_2O groups.

cluster in mcallisterite, aksaite and rivadite, (2) as the repeat unit in the infinite chain in aristarainite, and (3) in the infinite sheets of borate in the structures of nobleite, tunellite, strontioborite, ginorite (no determination of the structure to date) and strontioginorite (Grice *et al.* 1999). The FBB, 3Δ3□:<Δ2□>|<Δ2□>|Δ2□>|, does not exist in framework borates, but the all-tetrahedron variation, 6□:[ϕ]<3□>|<3□>|<3□>, is the FBB in the widely distributed boracite-group minerals.

Schindler & Hawthorne (2001) have formulated a method to determine the conditions of formation of borate minerals. They have calculated the topology of a pH – log[H_2O] diagram incorporating each of the borate structural units. Overlain on this topology, they have constructed two additional figures using the parameters: (a) average basicity (AB), and (b) percentage of tetrahedrally coordinated B ($^{[4]}$B). For the mineral assemblage at Sussex, New Brunswick, the AB (in valence units, *vu*) and $^{[4]}$B (%) for each mineral are: hilgardite (0.33, 60), strontioginorite (0.20, 43), trembathite (0.38, 86), volkovskite (0.23, 54), hydroboracite (0.37,66) and veatchite (0.25, 40). Applying these numbers to the relevant pH – log[H_2O] activity–activity diagram covers

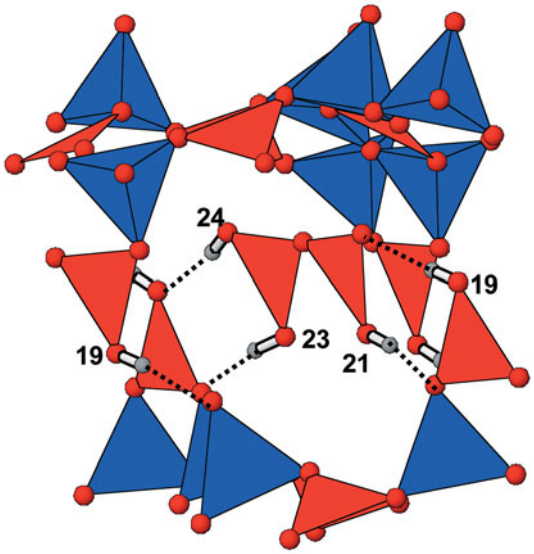

FIG. 4. Strontioginorite: [001] projection showing H-bonding within some of the OH^- groups.

a large proportion of the range of pH and log[H_2O]. This large range seems highly unlikely considering the close association of these minerals within the occurrence. Thus conditions of crystallization remains ambiguous with respect to pH and [H_2O] activity.

Strontioginorite, a highly polymerized borate-sheet structure, crystallizes late in the sequence within the Sussex deposits. It occurs with other highly polymerized borates such as volkovskite, hilgardite and trembathite. Among the associated borate minerals, strontioginorite is unique in having Sr as a major cation and no Cl.

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