CRYSTAL STRUCTURE OF STRONTIOGINORITE, $(Sr, Ca)_2B_{14}O_{20}(OH)_6 \cdot 5H_2O$[1]

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ABSTRACT

Determination of the structure of strontioginorite using a crystal of type material from Reyershausen, Germany, confirms the composition of the mineral as $2(Sr,Ca)O \cdot 7B_2O_3 \cdot 8H_2O$, and reveals that it contains a new kind of boron-oxygen polyanion, $[B_{14}O_{20}(OH)_6]^{4-}$. The crystal studied has a Sr:Ca ratio of 1 (by X-ray milliprobe analysis), is monoclinic, $P2_1/a$, with $a = 12.817$, $b = 14.448$, $c = 12.783$ Å (all ± 0.008 Å), $\beta = 101.42 \pm 0.08°$, $V = 2320$ Å³, $Z = 4[SrCaB_{14}O_{20}(OH)_6 \cdot 5H_2O]$, and density (calc.) $= 2.26_5$ g/cm³. Approximately 2800 hkl data were collected from the crystal by counter techniques, using CuKα radiation. The structure was solved by use of the symbolic addition method, together with successive electron-density difference syntheses, and study of a ball-and-stick model. Least-squares refinement reduced the conventional R to 6.4 percent for the 2350 data with $|F_0| > 4$ standard deviations (counting statistics). The $[B_{14}O_{20}(OH)_6]^{4-}$ polyanion is formed by corner-sharing between two crystallographically distinct tunellite-like polyanions, one of which has attached a linear side chain of composition $[B_2O_2(OH)_3]^{1-}$, the dimer of boric acid. The establishment of this type of polymerization significantly extends the principles governing the formation of complex boron-oxygen polyanions in crystals. The $[B_{14}O_{20}(OH)_6]^{4-}$ polyanions are linked into sheets parallel to (010); the sheets contain 8-coordinated Ca^{2+} and 10-coordinated Sr^{2+}. Water molecules lie between the layers and help hold them together through hydrogen bonding. The layers are directly linked by two Sr-OH bonds and by additional hydrogen bonds. The sheet structure is in accord with the (010) platy habit and perfect cleavage of the crystal.

INTRODUCTION

As part of a systematic study of borate minerals, we have continued our investigation of the crystal structures of minerals that occur in the system $MO–B_2O_3–H_2O$, where M represents a divalent cation. In the present paper we describe the crystal structure of a strontioginorite, $(Sr, Ca)_2B_{14}O_{20}(OH)_6 \cdot 5H_2O$, for which Sr:Ca = 1.

The name strontioginorite was given by Braitsch (1959) to the mineral discovered in the Königshall-Hindenberg salt mine, at Reyershausen, near Göttingen, Germany. Braitsch established that the mineral was a hydrated borate with Sr:Ca ratio of approximately 1.3:0.7. Scarcity of

TABLE 1. CRYSTALLOGRAPHIC DATA FOR STRONTIOGINORITE, GINORITE, AND VOLKOVITE

	Strontioginorite $SrCaB_{14}O_{20}(OH)_6$ $\cdot 5H_2O$ (Present study)	Strontioginorite $Sr_{1.3}Ca_{0.7}B_{14}O_{20}(OH)_6$ $\cdot 5H_2O$ (Braitsch, 1959)	Ginorite $Ca_2B_{14}O_{20}(OH)_6$ $\cdot 5H_2O$ (Kondrat'eva, 1963)	Volkovite $SrCaB_{14}O_{20}(OH)_6$ $\cdot 5H_2O(?)$ (Nefedov, 1953)
a (Å)	12.817 ± 0.008	12.85 ± 0.01	12.74 ± 0.01	12.93^e
b (Å)	14.448 ± 0.008	14.48 ± 0.01	14.36 ± 0.02	14.40
c (Å)	12.783 ± 0.008	12.85 ± 0.01	12.82 ± 0.02	12.79
β	$101°25' \pm 05'$	$101°35' \pm 10'$	$100°46' \pm 18'$	$100°27'$
Cell volume (Å^3)	2320	2340	2304	2342^e
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	—
Z	4	4	4	—
Density (g/cm^3) calc.	2.26_5	—	2.130	—
Density (g/cm^3) obs.	---	2.25	2.09^a 2.07^b	—

[a] D'Achiardi (1934).

[b] Allen and Kramer (1957).

[e] Nefedov gave a, b, c in kX units; conversion of these to Å units (1kX = 1.0026 Å) and volume calculation by present authors

material precluded a complete chemical analysis, but Braitsch assumed a composition $2(Sr, Ca)O \cdot 7B_2O_3 \cdot 8H_2O$, based on the close similarities of the powder pattern, optical properties, and density of the Reyershausen mineral to those of the mineral ginorite, for which the composition had previously been established as $2CaO \cdot 7B_2O_3 \cdot 8H_2O$ (D'Achiardi, 1934; Hey and Bannister, 1952; Allen and Kramer, 1957). More recently, Kondrat'eva (1963) determined the unit-cell constants and space group of ginorite by single-crystal X-ray studies, and again verified the close relationship of ginorite to strontioginorite. The assumed chemical composition for strontioginorite is confirmed by the present study in which the chemical formula of type material from Reyershausen is determined directly by the crystal structure analysis and by X-ray milliprobe analysis.

A third mineral, volkovite, originally considered by Nefedov (1953) to be a hydrous borate of Sr and K, was later described by him (Nefedov, 1955) as a hydrous Sr, Ca borate, containing approximately equal amounts of Sr and Ca, and related to ginorite. As was noted by Braitsch (1959), volkovite has single crystal X-ray and optical properties similar to those of strontioginorite. In Table 1, crystallographic data for strontioginorite, ginorite, and volkovite are compared.

The phase $2SrO \cdot 7B_2O_3 \cdot 8H_2O$ was synthesized in 1960 by R. C. Erd, U.S. Geological Survey (oral comm., 1960); it was found by him to have an X-ray powder pattern and optical properties similar to those of strontioginorite and ginorite. Erd's method of synthesis has been confirmed by Berdesinski and Meixner (1965). The mineral of composition $2SrO \cdot 7B_2O_3 \cdot 8H_2O$ is apparently not known.

Data are limited on the extent of solid solution between $2SrO \cdot 7B_2O_3 \cdot 8H_2O$ and $2CaO \cdot 7B_2O_3 \cdot 8H_2O$. The ginorite from Death Valley, Calif., described by Allen and Kramer (1957) was found by them to contain Sr, with $Ca:Sr = 1.9:0.1$. These authors point out that the Tuscany ginorites described by Hey and Bannister (1952) probably did contain small but significant amounts of Sr, although this was not reported. The ginorite from the Kungar formation in the Caspian Sea area studied by Kondrat'eva (1963) was reported not to contain Sr. In this laboratory, preliminary results of X-ray milliprobe analyses of four Reyershausen strontioginorite crystals indicate that the Sr:Ca ratio is variable around the 1:1 ratio. It is clear, from all of these results, that there can be at least limited mutual replacement between Sr and Ca near the Ca end-member, ginorite, and near the $Sr:Ca = 1$ composition, strontioginorite. There are no data on the substitution of Ca for Sr in $2SrO \cdot 7B_2O_3 \cdot 8H_2O$. As is discussed in greater detail subsequently, our structure analysis of the $Sr:Ca = 1$ crystal shows that Ca and Sr occupy distinct sites, Sr being 10-coordinated with an average Sr–O distance of 2.68 Å, and Ca, 8-coordinated with an average Ca–O distance of 2.51 Å. Taken at face value, these facts would indicate that variations in the Sr:Ca ratios in strontioginorite would be limited. However, the X-ray powder patterns of ginorite, strontioginorite, and the synthetic $2SrO \cdot 7B_2O_3 \cdot 8H_2O$ are quite similar. This similarity indicates that the structural variation is such as to preserve the main features of the structure while allowing for accommodation of the different sized Ca and Sr ions. On this basis, then, it is possible that solid solution can occur over a large part or all of the range from $2CaO \cdot 7B_2O_3 \cdot 8H_2O$ to $2SrO \cdot 7B_2O_3 \cdot 8H_2O$.

In the present paper, we have not concerned ourselves with problems of nomenclature and wish to defer to others the proper naming of the minerals concerned. However, it does not seem likely that this naming can be done objectively until the nature of the solid solution is known. We use the name strontioginorite for the phase whose crystal structure we have determined.

Experimental Data

Cell parameters, Symmetry, Physical and Chemical Properties. The crystal used for the structural study was a platy cleavage fragment, $0.27 \times 0.20 \times 0.06$ mm, cut from one of the large Reyershausen crystals described by Braitsch (1959) and supplied by him to R. C. Erd, U. S. Geological Survey, who in turn made it available to us. The monoclinic $P2_1/a$ symmetry reported by Braitsch (1959) was confirmed. The cell parameters determined in the present study are compared with those of Braitsch in Table 1. The density of strontioginorite, 2.25 g/cm³, measured by Braitsch, is in good agreement with the value of 2.26_5 g/cm³ calculated for $4[SrO \cdot CaO \cdot 7B_2O_3 \cdot 8H_2O]$, using the cell constants of the present study.

There was not enough of the Reyershausen material for a complete chemical analysis, but an X-ray milliprobe analysis for the Sr and Ca content of the crystal used in the structure analysis yielded the ratio Sr:Ca = 1. The analysis was made by H. J. Rose, Jr., and Ralph Christian, U. S. Geological Survey.

X-ray diffraction powder data were given by Braitsch (1959); refinement of these data by least-squares computer methods to obtain more precise cell parameters proved abortive because of the ambiguities in indexing caused by the small difference between a and c. New powder measurements could not be obtained due to the scarcity of material. Accordingly, lattice parameters were determined from precession film measurements, using calibrated crystal-to-film distances and shrinkage corrections. The errors listed in Table 1 are best estimates, based on repeated measurements by two observers

Of the six Reyershausen crystals available to us, two appear to be twinned. Braitsch (written comm., 1961) reported having found "twins of strontioginorite with [$\bar{1}$01] as twin axis". Possible twinning is being investigated presently, and the results will be reported elsewhere. The crystal used in the study of the structure was not twinned.

Data Collection, Processing and Refinement Procedures. The Picker automatic diffractometer with a scintillation counter was used for collection of about 2800 reflections with Ni-filtered Cu X-radiation set at a take-off angle of 3°. The 2θ-scan method was used, the scan range being calculated following the equation for CuKα radiation given by Alexander and Smith (1964), with constants adjusted slightly to increase the scan range. Background counts of 20 seconds duration were made for each reflection at the beginning and end of the scan range. The crystal was mounted with a^* parallel to the ϕ-axis, and the (212) reflection was monitored as a standard after each 30 measurements; some equivalent reflections were also checked.

Computer programs, written by C. T. Prewitt, SUNY, Stony Brook, and modified by D. E. Appleman, U. S. Geological Survey, for the IBM 360/65, were used to obtain the diffractometer settings and to reduce the raw data, including corrections for the total background count, absorption ($\mu = 67.1$ cm^{-1}), and Lorentz and polarization factors (program ACACA). No corrections were made for extinction, either primary or secondary; the data appeared to be relatively unaffected by primary extinction. Reflections for which $|F_0|$ was less than four times the standard deviation in $|F_0|$ as determined by the counting statistics numbered 456. These data were coded as "less-thans" and omitted during the refinements, which used 2350 nonequivalent reflections.

Computer programs from X-Ray 67, *Program System for X-Ray Crystallography*, by J. M. Stewart, University of Maryland, adapted for the IBM 360/65 by D. E. Appleman, U. S. Geological Survey, were used for obtaining normalized structure factors, for determination of phases, and for calculations of Fourier syntheses and least-squares planes. Programs written by L. W. Finger, Geophysical Laboratory, Washington, D. C., were used for least-squares and site occupancy refinements, and calculations of bond distances, bond angles and thermal ellipsoids. Because of the large number of atoms (47), only individual, isotropic thermal parameters were refined for boron and oxygen atoms. Anisotropic thermal parameters were determined for Sr and Ca in the final cycles. The atomic scattering factors used in the calculations were obtained from a nine coefficient analytical function (Cromer and Waber, 1965), using the coefficients of Doyle and Turner (1968, Table 3) for neutral oxygen and boron, Ca^{2+} and Sr^{2+}. Anomalous dispersion corrections were included in the calculations. Unit weights were used throughout the refinements.

DETERMINATION OF THE STRUCTURE

The structural problem consisted of locating one Sr, one Ca, 14 boron and 31 oxygen atoms in the general fourfold positions 4e of space group $P2_1/a$. A three-dimensional Pat-

TABLE 2. STATISTICAL AVERAGES AND DATA PERTINENT TO
SIGN DETERMINATION FOR STRONTIOGINORITE

Normalized Structure Factors	Averages		
	Experimental	Theoretical	
		Centrosymmetic	Acentric
$\langle \lvert E \rvert \rangle$	0.783	0.798	0.886
$\langle \lvert E^2-1 \rvert \rangle$	0.992	0.968	0.736
$\langle \lvert E^2 \rvert \rangle$	1.000	1.000	1.000
	Distribution (%)		
$\lvert E \rvert > 3.0$	0.3	0.3	0.0
$\lvert E \rvert > 2.0$	4.4	4.6	1.8
$\lvert E \rvert > 1.0$	30.3	31.7	36.8

Signs Fixed to Determine Origin

$h \ k \ l$	$\lvert E \rvert$	F_{obs}
2, 12, $\bar{7}$	2.28	+103
5, 5, $\overline{11}$	3.91	+153
2 1 $\bar{6}$	4.34	+387

terson synthesis was calculated, from which the Sr position was readily determined and a Ca position tentatively assigned. However, because the X-Ray 67 PHASE program was also available, it was used independently to obtain phases, and no further study was made of the Patterson. The PHASE program is based on the symbolic addition method for centrosymmetric structures (Karle and Karle, 1966), and uses the normalized structure factors E_{hkl}. The statistical averages obtained for the data are given in Table 2 and confirm the centrosymmetric assignment. The signs of three reflections were chosen positive to fix the origin (Table 2), following the procedures described by Hauptman and Karle (1953). The PHASE program was instructed to use reflections with $\lvert E \rvert \geq 1.5$ and relationships with probabilities greater than 0.95; a total of 339 signs were unambiguously determined and an E-map calculated. The Sr position obtained from the Patterson synthesis was confirmed, but the tentative Ca assignment similarly made turned out to be incorrect. The true Ca position (peak height 516) was apparent on the E-map and ten other well defined peaks (heights 146 to 237) were assumed to represent oxygen atoms. A difference Fourier synthesis using calculated structure factors for Sr+Ca+10 oxygens showed that two of the ten oxygens which had peak heights above 200 on the E-map were incorrect, but new peaks permitted addition of eleven oxygens and two boron atoms to the known list. Study of a second difference synthesis based on calculated structure factors for Sr+Ca+19 oxygens +2B revealed the locations of three more oxygen and nine more boron atoms. At this stage in the determination, work with a ball-and-stick model led to identification of two linked polyanion units, each one similar to the $[B_6O_9(OH)_2]^{2-}$ polyanion found in tunellite (Clark, 1963). The linked pair appeared to be related by a pseudo c-glide and formed infinite sheets

parallel to (010). A third difference synthesis indicated the presence of three water mole-
cules, plus a $[B_2O_2(OH)_3]^{1-}$ chain attached to one of the two tunellite-like polyanions and so
removing the pseudo c-glide previously observed. A fourth difference synthesis revealed the
remaining two water molecules.

The conventional residual, $R = (\sum ||F_0| - |F_c||)/\sum |F_0|$, for the 2350 reflections with
$|F_0| > 4$ standard deviations was 0.53 for the $Sr + Ca + 10$ oxygens initially assigned. With
all atoms located, it dropped to 0.25, and after two least-squares cycles refining positional
parameters followed by two cycles refining positional parameters and individual isotropic
temperature factors, R became 0.079. Two further cycles, refining these parameters and
anisotropic thermal parameters for Sr and Ca only, lowered the final R to 0.064. The final
so-called weighted $R = [\sum w(|F_0| - |F_0|)^2/\sum w|F_0|^2]^{\frac{1}{2}}$ with $w = 1$ is 0.070. At this stage
of the procedure, a site occupancy refinement for the Sr:Ca ratio was carried out without
restricting the total amounts of either cation, but assuming fully occupied sites; no change
in R resulted, and the Sr:Ca ratio calculated to unity. A final difference synthesis was rela-
tively featureless. The final parameters are given in Table 3, and the observed and calcu-
lated structure factors are compared in Table 4.[1] The anisotropic thermal parameters and
resultant ellipsoids for Sr and Ca are given in Table 5.

DESCRIPTION OF THE STRUCTURE

Consistent with the platy habit and good (010) cleavage of the crystals,
strontioginorite has a sheet structure. A stereoscopic pair view of the
structure is shown in Figure 1; a preliminary description was given by
Konnert, Clark and Christ (1970). The thick sheets parallel to (010)
contain both Sr and Ca cations held in a framework of polymerized
borate polyanions. Adjacent sheets are related by the 2_1-symmetry axis.
Water molecules located between adjacent sheets form hydrogen bonds
among themselves and to hydroxyls of the sheets. The sheets are held
together by two Sr–OH bonds, and by hydrogen bonds among hy-
droxyls and water molecules; the structural formula of strontioginorite
is $SrCaB_{14}O_{20}(OH)_6 \cdot 5H_2O$. Discussion of the structure, given in the
following, is divided into these sections: the polyanion sheets, including
the Sr and Ca coordination; the intersheet linkages, including the hydro-
gen bonding and water molecule environments; and charge balance
considerations.

Polyanion Sheets. A schematic drawing is given in Figure 2 of the crystal-
lographic unit that repeats to form the polyanion sheets of strontioginor-
ite. The portions of this unit labelled I and II are each similar
to the polyanion first found in polymerized form in tunellite,
$SrB_6O_9(OH)_2 \cdot 3H_2O$ (Clark, 1963, 1964), and recently discovered in

[1] Table 4 may be ordered as NAPS Document No. 01112 from National Auxiliary Publi-
cation Service of A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New
York, N. Y. 10022, remitting in advance $2.00 for microfiche or $7.30 for photocopies,
payable to ASIS-NAPS. The final standard deviation in $|F|$ is 11.8.

TABLE 3. ATOMIC AND ISOTROPIC TEMPERATURE PARAMETERS FOR STRONTIOGINORITE

Structural element[a]		Parameters[b]				
Polyanion (See Fig. 2)	Ring	Atom	x	y	z	$B(Å^2)$
		Sr	0.6178(1)	0.1711(1)	0.7364(1)	1.25[c]
		Ca	.1264(1)	.2187(1)	.2463(1)	0.73[c]
I	1,2	B(1)	.3903(8)	.2010(7)	−.1236(8)	0.7(2)
	1,3	B(2)	.4334(8)	.3031(7)	.0504(8)	1.0(2)
	2,3	B(3)	.2622(8)	.1961(7)	.0125(8)	0.8(2)
	1	B(4)	.5752(8)	.2551(7)	−.0426(8)	0.7(2)
	3	B(5)	.3410(8)	.2573(7)	.1920(8)	0.8(2)
	2	B(6)	.3046(9)	.0571(7)	−.0796(8)	1.1(2)
	1,2,3	O(1)	.3667(4)	.2306(4)	−.0165(4)	0.6(1)
	3	O(2)	.4324(5)	.2890(4)	.1635(5)	1.0(1)
	3	O(3)	.2627(5)	.2156(4)	.1239(5)	1.0(1)
	2	O(4)	.2574(5)	.0967(4)	−.0046(5)	1.2(1)
	2	O(5)	.3645(5)	.1038(4)	−.1369(5)	1.1(1)
	1	O(6)	.5032(5)	.2121(4)	−.1213(5)	1.0(1)
	1	O(7)	.5443(5)	.2942(4)	.0439(5)	1.2(1)
		OH(8)	.2923(5)	−.0375(5)	−.1003(5)	2.1(1)
		OH(9)	.3876(5)	.3922(4)	.0146(5)	1.7(1)
I,I′	linking	O(10)	.1774(5)	.2449(4)	−.0557(5)	1.2(1)
I,II	linking	O(11)	.3221(5)	.2682(4)	.2933(5)	0.9(1)
II	1,2	B(7)	.3902(8)	.3189(7)	.3781(8)	0.7(2)
	1,3	B(8)	.4223(8)	.2021(7)	.5384(8)	0.9(2)
	2,3	B(9)	.2549(8)	.3110(7)	.5049(8)	0.8(2)
	1	B(10)	.5704(8)	.2546(7)	.4567(8)	0.8(2)
	3	B(11)	.3364(8)	.2530(7)	.6868(7)	0.5(2)
	2	B(12)	.2922(8)	.4571(7)	.4152(8)	0.8(2)
	1,2,3	O(12)	.3628(4)	.2839(4)	.4816(5)	0.5(1)
	3	O(13)	.4122(5)	.2040(4)	.6507(5)	0.9(1)
	3	O(14)	.2589(5)	.3007(4)	.6183(4)	0.9(1)
	2	O(15)	.2349(5)	.4071(4)	.4757(4)	0.9(1)
	2	O(16)	.3680(5)	.4175(4)	.3694(5)	1.0(1)
	1	O(17)	.5030(5)	.3049(4)	.3809(4)	0.8(1)
	1	O(18)	.5358(5)	.2136(4)	.5399(5)	0.9(1)
		OH(19)	.2707(5)	.5488(5)	.3972(5)	1.9(1)
II, side chain	linking	O(20)	.3810(5)	.1160(4)	.4898(5)	1.0(1)
II,II′	linking	O(25)	.1729(5)	.2518(4)	.4419(4)	0.9(1)
II,I″	linking	O(26)	.3285(5)	.2568(4)	.7919(5)	1.0(1)
Side chain	none	B(13)	.4099(8)	.0668(7)	.4092(8)	0.9(2)
		B(14)	.5247(8)	.0623(7)	.2736(8)	0.9(2)
		OH(21)	.3730(5)	−.0219(4)	.3899(5)	1.5(1)
		O(22)	.4742(5)	.1041(4)	.3465(5)	1.3(1)
		OH(23)	.5046(5)	−.0264(5)	.2415(5)	1.8(1)
		OH(24)	.5952(5)	.1170(4)	.2329(5)	1.5(1)
Water molecules		$H_2O(1)$	.1096(6)	.1489(5)	.7207(6)	2.3(1)
		$H_2O(2)$	.1537(6)	.0614(5)	.2715(6)	2.6(1)
		$H_2O(3)$	.2367(5)	.4502(5)	.8493(5)	2.1(1)
		$H_2O(4)$	.0167(6)	.0384(5)	.8661(6)	2.8(1)
		$H_2O(5)$	.0509(6)	−.0246(5)	.4008(6)	2.8(1)

[a] Unprimed polyanion related to single-primed polyanion by a-glide, and to double-primed polyanion by c-translation.

[b] Errors in parentheses are for one standard deviation, *e.g.*, 0.6178(1) means 0.6178 ± 0.0001, *etc.*

[c] Equivalent isotropic B calculated from anisotropic parameters (see Table 5).

TABLE 5. ANISOTROPIC THERMAL PARAMETER TENSOR VALUES;
THERMAL ELLIPSOIDS FOR SR AND CA IN STRONTIOGINORITE

Anisotropic Thermal Parameters		
Tensor	Tensor value $\times 10^4$	
	Sr	Ca
β_{11}[a]	26.5 (7)[b]	15 (1)
β_{22}	12.0 (5)	7 (1)
β_{33}	20.1 (6)	13 (1)
β_{12}	0.8 (4)	−2 (1)
β_{13}	12.2 (5)	8 (1)
β_{23}	1.3 (4)	0 (1)

Thermal Ellipsoids (axes r_i)

	Sr			Ca		
	r_1	r_2	r_3	r_1	r_2	r_3
Amplitudes (Å)	0.102 (2)	0.113 (2)	0.156 (2)	0.072 (6)	0.091 (5)	0.120 (4)
Angle (°) of r_i with: a	126 (3)	76 (6)	40 (2)	132 (6)	77 (10)	44 (5)
b	106 (9)	163 (8)	84 (2)	117 (13)	152 (13)	98 (7)
c	31 (4)	102 (8)	62 (2)	44 (9)	116 (12)	58 (5)

[a] Thermal parameter form: $\exp\left\{-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right\}$.

[b] Errors in parentheses are for one standard deviation; *e.g.*, 26.5 (7) means 26.5 ± 0.7.

isolated form, $[B_6O_7(OH)_6]^{2-}$, in the crystal structure of macallisterite, $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$ (Dal Negro, Sabelli and Ungaretti, 1969). The tunellite polyanion consists of three B–O tetrahedra and three B–O triangles connected at corners, and having the characteristic linkage of a central oxygen to the borons of the three tetrahedra. In I of Figure 2, the central oxygen is O(1), and in II is O(12). Oxygens linked to only one boron attach a proton, following the third rule of Christ (1960), so that in the monomer form each triangle and each tetrahedron has one hydroxyl ion. In the crystal structure of macallisterite (space group $R\bar{3}c$), the central oxygen is located on a threefold axis, so that the monomer in the structure has exact trigonal symmetry. In tunellite and in strontioginorite, polymerization has occurred following the fourth rule of Christ (1960) to produce polyanion sheets. As Figure 2 shows, strontioginorite has two such polyanions (I and II), crystallographically distinct,
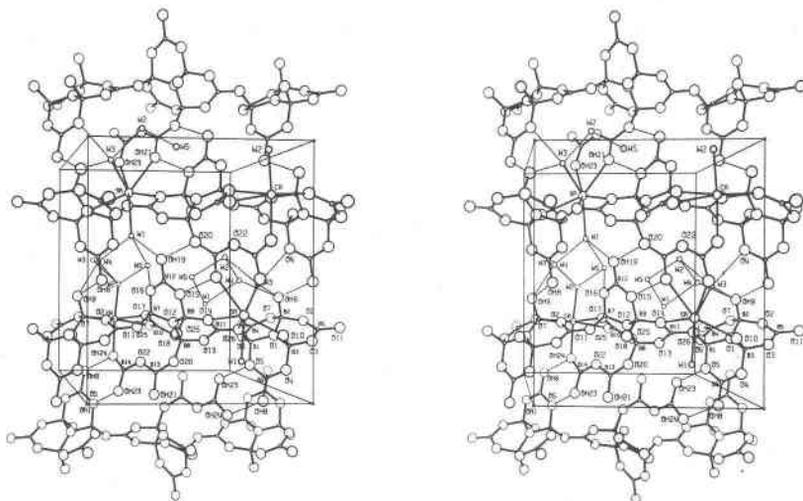
Fig. 1. Stereoscopic pair view along a^* of the strontioginorite structure, showing the stacking of the polyanion sheets and the intersheet linkages. Atoms are labelled in one of the four polyanion sheets illustrated; W is used for the H_2O (Table 3). The outline of one unit cell is shown, origin marked ORI, c horizontal, b vertically up, and a into the paper. Drawing produced with ORTEP (Johnson, 1965).
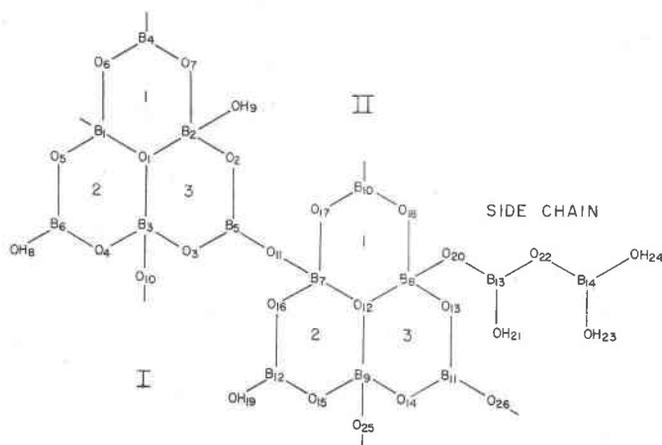
Fig. 2. Schematic diagram of the $[B_{14}O_{20}(OH)_6]^{4-}$ polyanion, oriented as in Fig. 3, lower left. Tunellite-like polyanions marked by Roman numerals and rings by Arabic numerals. Sheet linkages as follows: $O(26)$ to a $B(1)$ translated by c; $B(4)$ to an $O(10)$ translated by the a glide; $B(10)$ to an $O(25)$ also translated by the a glide.

joined in pairs through a common oxygen, O(11). The pairs are linked into chains by sharing oxygens, O(26) and its counterparts along the c axis. The chains are joined into sheets by sharing oxygens O(10) and O(25) through their a-glide equivalents.

To complete the strontioginorite polyanion, a polymerized side chain of boric acid, $[B_2O_2(OH)_3]^{1-}$, has attached to one of the two larger polyanions at O(20), producing the full sheet of composition $[B_{14}O_{20}(OH)_6]^{4-}$, illustrated in Figure 3 as it appears in the structure. A similar, smaller side chain of boric acid, $[BO(OH)_2]^{1-}$ is part of the polyanion $[B_6O_8(OH)_5]^{3-}$ found in the crystal structure of kaliborite, $HKMg_2$ $[B_6O_8(OH)_5]_2 \cdot 4H_2O$ (Corazza and Sabelli, 1966). Isolated boric acid

STRONTIOGINORITE POLYANION   STRONTIOGINORITE POLYANION
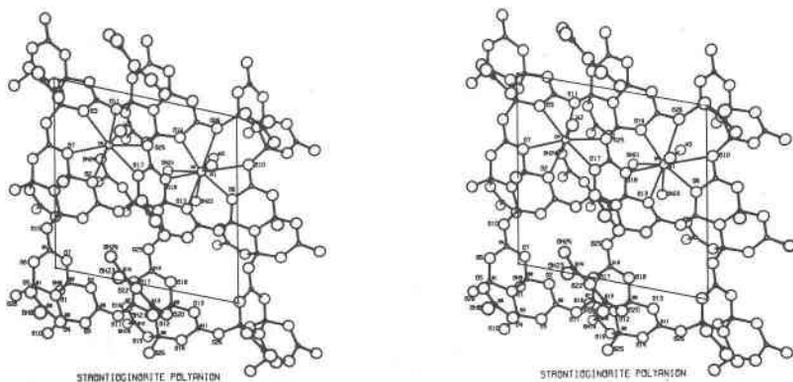
Fig. 3. Stereoscopic pair view along $-b$ of one polyanion sheet showing coordination for one Sr and one Ca. Symmetric counterparts of Sr and Ca have been omitted for clarity. The outline of the (010) plane is shown with origin at lower left, c along the horizontal. W is used to designate H_2O (Table 3). Drawing produced with ORTEP (Johnson, 1965).

groups, $B(OH)_3$, have been found in the crystal structures of veatchite (Clark and Christ, 1968) and p-veatchite (Gandimov, Rumanova and Belov, 1968), both minerals of composition $Sr_2[B_5O_8(OH)]_2$ $\cdot B(OH)_3 \cdot H_2O$.

The boron-oxygen distances in the strontioginorite polyanions are listed in Table 6; the average for all tetrahedral B–O is 1.47 Å, for all triangular B–O, 1.37 Å, in good agreement with those found in other borate structures. Oxygen-oxygen distances average 2.36 Å in the triangles and 2.40 Å in the tetrahedra. As in both tunellite and macallisterite, the average of 1.52 Å for those B–O distances involving the central oxygens is somewhat longer than the usual 1.47 Å value for tetrahedral B–O, again confirming the prediction made by Zachariasen (1963) for the B–O distance of an oxygen linked to three borons. The

TABLE 6. BORON-OXYGEN BOND LENGTHS IN STRONTIOGINORITE (See Figs. 2 and 3)

Ring No.	Atoms in Polyanion No.		Bond Length (Å)[a] Polyanion No.	
	I	II	I	II
	Tetrahedra			
1, 2	B(1)–O(1)	B(7)–O(12)	1.52	1.52
	–O(5)	–O(16)	1.45	1.45
	–O(6)	–O(17)	1.45	1.45
	–O(26)	–O(11)	1.45	1.45
			Av. 1.47	1.47
1, 3	B(2)–O(1)	B(8)–O(12)	1.51	1.51
	–O(2)	–O(13)	1.46	1.47
	–O(7)	–O(18)	1.45	1.46
	–OH(9)	–O(20)	1.45	1.44
			Av. 1.47	1.47
2, 3	B(3)–O(1)	B(9)–O(12)	1.54	1.52
	–O(3)	–O(14)	1.45	1.45
	–O(4)	–O(15)	1.45	1.45
	–O(10)	–O(25)	1.44	1.47
			Av. 1.47	1.47
	Overall average tetrahedra 1.47 Å			
	Triangles			
1	B(4)–O(6)	B(10)–O(17)	1.37	1.37
	–O(7)	–O(18)	1.37	1.37
	–O(10)	–O(25)	1.35	1.37
			Av. 1.36	1.37
2	B(6)–O(4)	B(12)–O(15)	1.36	1.37
	–O(5)	–O(16)	1.34	1.36
	–OH(8)	–OH(19)	1.40	1.36
			Av. 1.37	1.36
3	B(5)–O(2)	B(11)–O(13)	1.37	1.36
	–O(3)	–O(14)	1.33	1.37
	–O(11)	–O(26)	1.37	1.37
			Av. 1.36	1.37
	Side Chain Triangles			
	B(13)–O(20)	B(14)–O(22)	1.36	1.37
	–O(22)	–OH(23)	1.37	1.36
	–OH(21)	–OH(24)	1.37	1.38
			Av. 1.37	1.37
	Overall average, triangles 1.37 Å			

[a] The average error in the B–O distances is ±0.01 Å, corresponding to one standard deviation.

Ring	Bond, polyanion		Angle (°)[a], polyanion	
	I	II	I	II
	Tetrahedra			
1, 2	O(1)–B(1)–O(5)	O(12)–B(7)–O(16)	107.3(7)	108.6(7)
	O(1)–B(1)–O(6)	O(12)–B(7)–O(17)	109.0(7)	109.4(7)
	O(1)–B(1)–O(26)	O(12)–B(7)–O(11)	109.7(7)	105.8(7)
	O(5)–B(1)–O(6)	O(16)–B(7)–O(17)	108.3(7)	108.5(7)
	O(5)–B(1)–O(26)	O(16)–B(7)–O(11)	111.9(8)	111.0(7)
	O(6)–B(1)–O(26)	O(17)–B(7)–O(11)	110.5(7)	113.4(7)
1, 3	O(1)–B(2)–O(2)	O(12)–B(8)–O(13)	110.4(7)	108.8(7)
	O(1)–B(2)–O(7)	O(12)–B(8)–O(18)	111.1(7)	108.9(7)
	O(1)–B(2)–OH(9)	O(12)–B(8)–O(20)	106.8(7)	111.1(7)
	O(2)–B(2)–O(7)	O(13)–B(8)–O(18)	104.3(8)	105.4(7)
	O(2)–B(2)–OH(9)	O(13)–B(8)–O(20)	110.7(8)	110.0(7)
	O(7)–B(2)–OH(9)	O(18)–B(8)–O(20)	113.7(8)	112.5(8)
2, 3	O(1)–B(3)–O(3)	O(12)–B(9)–O(14)	109.8(7)	108.4(7)
	O(1)–B(3)–O(4)	O(12)–B(9)–O(15)	107.2(7)	108.5(7)
	O(1)–B(3)–O(10)	O(12)–B(9)–O(25)	106.6(7)	108.9(7)
	O(3)–B(3)–O(4)	O(14)–B(9)–O(15)	109.4(7)	109.0(7)
	O(3)–B(3)–O(10)	O(14)–B(9)–O(25)	110.9(8)	111.7(7)
	O(4)–B(3)–O(10)	O(15)–B(9)–O(25)	112.9(8)	110.3(7)
	Triangles			
1	O(6)–B(4)–O(7)	O(17)–B(10)–O(18)	121.2(8)	121.6(8)
	O(6)–B(4)–O(10)	O(17)–B(10)–O(25)	116.0(8)	115.3(8)
	O(7)–B(4)–O(10)	O(18)–B(10)–O(25)	122.8(8)	123.2(8)
		Σ	360.0	360.1
2	O(4)–B(6)–O(5)	O(15)–B(12)–O(16)	123.9(9)	122.0(8)
	O(4)–B(6)–OH(8)	O(15)–B(12)–OH(19)	119.9(9)	119.5(8)
	O(5)–B(6)–OH(8)	O(16)–B(12)–OH(19)	116.3(8)	118.4(8)
		Σ	360.1	359.9
3	O(2)–B(5)–O(3)	O(13)–B(11)–O(14)	123.2(8)	121.5(8)
	O(2)–B(5)–O(11)	O(13)–B(11)–O(26)	122.1(8)	123.5(8)
	O(3)–B(5)–O(11)	O(14)–B(11)–O(26)	114.6(8)	115.0(8)
		Σ	359.9	360.0
	Side Chain Triangles			
	O(20)–B(13)–O(22)	O(22)–B(14)–OH(23)	121.6(9)	122.3(9)
	O(20)–B(13)–OH(21)	O(22)–B(14)–OH(24)	119.1(8)	115.8(8)
	O(22)–B(13)–OH(21)	OH(23)–B(14)–OH(24)	119.3(8)	121.9(8)
		Σ	360.0	360.0
	Ring Angles			
1	B(1)–O(1)–B(2)	B(7)–O(12)–B(8)	121.0(7)	119.8(7)
	B(2)–O(7)–B(4)	B(8)–O(18)–B(10)	121.9(7)	121.0(7)
	B(4)–O(6)–B(1)	B(10)–O(17)–B(7)	126.1(7)	125.1(7)
2	B(1)–O(1)–B(3)	B(7)–O(12)–B(9)	117.6(6)	117.4(6)
	B(3)–O(4)–B(6)	B(9)–O(15)–B(12)	120.8(7)	124.3(7)
	B(6)–O(5)–B(1)	B(12)–O(16)–B(7)	124.4(7)	121.8(7)
3	B(2)–O(1)–B(3)	B(8)–O(12)–B(9)	120.7(7)	119.9(7)
	B(3)–O(3)–B(5)	B(9)–O(14)–B(11)	125.8(7)	124.6(7)
	B(5)–O(2)–B(2)	B(11)–O(13)–B(8)	119.0(7)	123.4(7)
		Av.	121.9	121.9

[a] Errors in parentheses are for one standard deviation, e.g. 107.3(7) means 107.3 ± 0.7°.

TABLE 8. BORON-BORON DISTANCES IN STRONTIOGINORITE (See Figs. 2 and 3)

Ring No.	Number of Boron in Polyanion		B–B Distance (Å)[a], Polyanion	
	I	II	I	II
1	(1)–(2)	(7)–(8)	2.63	2.62
	(1)–(4)	(7)–(10)	2.52	2.51
	(2)–(4)	(8)–(10)	2.46	2.46
2	(1)–(3)	(7)–(9)	2.62	2.60
	(1)–(6)	(7)–(12)	2.47	2.45
	(3)–(6)	(9)–(12)	2.44	2.49
3	(2)–(3)	(8)–(9)	2.65	2.63
	(2)–(5)	(8)–(11)	2.44	2.49
	(3)–(5)	(9)–(11)	2.48	2.50
Linking to adjacent polyanions[b]				
	I, II	(5)–(7)	2.50	
	I, II''	(1)–(11)	2.50	
	I, I'	(3)–(4)	2.46	
	II, II'	(9)–(10)	2.51	
In the side chain				
		(8)–(13)	2.54	
		(13)–(14)	2.49	
Average B–B distances (Å)				
Overall average for 24				2.52
Average for 6 tetrahedron-tetrahedron				2.63
Average for 17 tetrahedron-triangle				2.48
Triangle-triangle (side chain)				2.49

[a] Average error in B–B distances is ± 0.01Å, corresponding to one standard deviation.
[b] Unprimed polyanion related to single-primed polyanion by a-glide, and to double-primed polyanion by c-translation.

angles in the polyanions are given in Table 7 and fall within expected values; the triangles are planar within the limits of error. Boron-boron distances are listed in Table 8; the average B–B distance within the $[B_{14}O_{20}(OH)_6]^{4-}$ polyanion is 2.52 Å; the average B–B distance involved in cross-linking to form the sheets is 2.49 Å.

Equations for the planes of the three oxygen atoms in each of the six-membered rings of the strontioginorite polyanions are given in Table 9. For the polyanions of strontioginorite, tunellite, and macallisterite, the distances of the borons and the remaining triangle oxygen or hydroxyl from the planes are given in Table 10, and the angles between various planes are given in Tables 11 and 12. The deviations from

planarity do not exceed a maximum of about 0.5 Å for any ring atom
(Table 10), whether its polyanion is isolated or linked. Bending of ring
planes about the central oxygen increases from 18° in the macallisterite
polyanion to a maximum of about 37° in strontioginorite polyanion I
(Table 11). In both polyanions I and II in strontioginorite, rings 1 and
3 deviate less from coplanarity than does ring 2 from rings 1 and 3.
Reference to Figure 1 shows that the deviation of ring 2 alternates in I
and II in such fashion that the triangle hydroxyls OH(8) of I and OH(19)
of II can form hydrogen bonds between adjacent sheets.

The Ca and Sr cations must be considered as belonging to the sheets,
because the cations fit into spaces of the large polyanion (Fig. 3) and
are coordinated primarily within one sheet. The cation-oxygen distances

TABLE 9. EQUATIONS OF PLANES FOR OXYGEN ATOMS OF RINGS IN THE STRONTIOGINORITE
POLYANIONS (See Fig. 2)

Ring	Coefficients of Equation[a]					
	Polyanion I			Polyanion II		
	P	Q	L	P	Q	L
1	−1.277	6.174	−2.751	0.368	1.612	0.849
2	5.505	−4.115	4.235	0.752	0.829	1.022
3	−4.305	11.039	−2.009	0.889	1.569	0.482

[a] $Px + Qy + Lz = 1$ where x, y, z are atomic coordinates (Table 3).

are given in Table 13. Ca is 8-coordinated by one water molecule, plus
six oxygens and one hydroxyl ion within one sheet. The Ca–O dis-
tances range from 2.313 to 2.600 Å; the average is 2.504 Å, somewhat
higher than average Ca–O distances in the structures of the 2CaO
$\cdot 3B_2O_3 \cdot xH_2O$ series of borates (Clark, Appleman, and Christ, 1964),
but within the sum of effective ionic radii for 8-coordination, given as
2.52 Å by Shannon and Prewitt (1969). Sr is 10-coordinated by two water
molecules, two hydroxyl ions from a side chain in one sheet, and six
oxygens from a second adjacent sheet. The Sr–O distances range from
2.570 to 2.884 Å; the average is 2.680 Å, slightly less than the 2.736 Å
average found for the 10-coordinated Sr in tunellite. However, 10-
coordinated Sr has been reported in the structure of $Sr_3(PO_4)_2$ with an
average value of 2.67 Å (Zachariasen, 1948)[1] and in the structure of
$Sr(MnO_4)_2 \cdot 3H_2O$ with an average value of 2.677 ± 0.074 Å (Ferrari

[1] This example was overlooked by Clark (1964) who reported tunellite as the first
tructure having 10-coordinated Sr.

TABLE 10. COMPARISON OF PLANARITY OF RINGS IN STRONTIOGINORITE, TUNELLITE, AND MACALLISTERITE

Ring	Oxygens Defining Ring[a]		Distance (Å) of Atoms from Plane Defined by Ring Oxygens[b]							
	Tunellite (Clark, 1964)	Macallisterite (Dal Negro et al., 1969)	Strontioginorite (Present study)				Tunellite (Clark, 1964)		Macallisterite (Dal Negro et al., 1969)	
			Polyanion I		Polyanion II					
1	O(1), O(9)″, O(14)	O(7), O(3)′, O(4)	B(1)	0.16	B(7)	−0.16	B(1)	−0.33	B(1)	0.27
			B(2)	0.36	B(8)	−0.45	B(4)″	−0.26	B(1)′	0.49
			B(4)	−0.09	B(10)	0.06	B(6)″	0.11	B(2)	−0.19
			O(10)	−0.27	O(25)	0.17	O(8)	0.43	OH(6)	−0.51
2	O(2), O(7)″, O(14)		B(1)	−0.30	B(7)	−0.45	B(2)	−0.16		
			B(3)	−0.46	B(9)	−0.28	B(4)″	−0.48		
			B(6)	0.16	B(12)	0.18	B(5)″	0.10		
			OH(8)	0.51	OH(19)	0.52	O(6)	0.29		
3	O(10), O(11), O(14)		B(2)	0.44	B(8)	−0.35	B(1)	−0.25		
			B(3)	0.01	B(9)	−0.30	B(2)	−0.32		
			B(5)	−0.02	B(11)	0.19	B(3)	0.03		
			O(11)	−0.02	O(26)	0.55	OH(3)′	0.13		

[a] For ring designations in strontioginorite see Fig. 2 In macallisterite O(7) is located on a threefold axis so that the three rings are symmetry equivalents.

[b] Average errors in distances are: for strontioginorite, ±0.02 Å; for tunellite, ±0.03 Å; for macallisterite ±0.01 Å, all corresponding to one standard deviation.

TABLE 11. ANGLES BETWEEN PLANES OF POLYANION RINGS COMPARED FOR
STRONTIOGINORITE, TUNELLITE AND MACALLISTERITE POLYANIONS
(See Fig. 2 and Tables 9 and 10)

Ring Nos.	Angles (°)		Tunellite[a] (Clark, 1964)	Macallisterite[b] (Dal Negro et al., 1969)
	Strontioginorite (Present study)			
	Polyanion I	Polyanion II		
1 to 2	37.1	28.3	27	17.8
1 to 3	16.6	19.1	28	17.8
2 to 3	37.4	28.5	33	17.8

[a] Supplements of those given in reference.

[b] Calculated by present authors from data in reference.

et al., 1966). The cation polyhedra are isolated and do not share corners
or edges with one another or with symmetry-related counterparts.

Intersheet Linkage, Hydrogen Bonds and Water Molecule Environments.
Adjacent sheets are held together directly by: (1) the linkage of Sr by hy-
droxyls in successive sheets, as already described, and (2) by five hydro-
gen bonds involving six hydroxyl ions in two different sheets. Additional
linkages occur through two water molecules, $H_2O(1)$ and $H_2O(3)$, which
each coordinate Sr in one layer and form hydrogen bonds with, respec-
tively, OH(19) and O(4) in the adjacent layer (Fig. 1). The other three

TABLE 12. ANGLES BETWEEN PLANE OF TRIANGLE OXYGENS AND PLANE OF RING OXYGENS
COMPARED FOR STRONTIOGINORITE, TUNELLITE AND MACALLISTERITE POLYANIONS
(See Fig. 2 and Tables 9 and 10)

Ring No. or Triangle Boron	Angle (°)		Tunellite[a] (Clark, 1964)	Macallisterite[a] (Dal Negro et al., 1969)
	Strontioginorite (Present study)			
	Polyanion I	Polyanion II		
1	7.8	4.8	12	14.8
2	14.5	14.8	8	14.8
3	0.5	15.7	4	14.8
Side chain ΔB(13)				
to ring 1	—	78.2		
to ring 3	—	71.7		
ΔB(13) to ΔB(14)	8.3			

[a] Calculated by present authors from data in reference.

TABLE 13. CALCIUM AND STRONTIUM COORDINATION IN STRONTIOGINORITE (See Fig. 3)

Atom	Oxygen Atom Location			Ca-O Distance (Å)[a]
	x	y	z	
O(2)	−0.0676	0.2111	0.1635	2.504(7)
O(3)	0.2628	0.2156	0.1239	2.567(6)
O(7)	0.0443	0.2058	0.0439	2.600(7)
O(11)	0.3221	0.2682	0.2933	2.563(6)
O(17)	0.0030	0.1951	0.3809	2.579(6)
OH(24)	0.0952	0.3830	0.2329	2.407(7)
O(25)	0.1729	0.2518	0.4419	2.499(6)
$H_2O(2)$	0.1537	0.0614	0.2715	2.313(8)
				Mean 2.504
				Sr-O Distance (Å)[a]
O(6)	0.5032	0.2121	0.8787	2.623(6)
O(10)	0.6774	0.2552	0.9444	2.884(6)
O(13)	0.4122	0.2040	0.6507	2.689(7)
O(14)	0.7589	0.1993	0.6183	2.606(6)
O(18)	0.5358	0.2136	0.5399	2.598(7)
OH(21)	0.6270	0.0219	0.6101	2.710(6)
OH(23)	0.4954	0.0264	0.7585	2.663(7)
O(26)	0.8285	0.2432	0.7919	2.849(6)
$H_2O(1)$	0.6096	0.3511	0.7207	2.608(7)
$H_2O(3)$	0.7367	0.0498	0.8493	2.570(7)
				Mean 2.680

[a] xyz coordinates of Ca and Sr given in Table 3. Errors in parentheses are for one standard deviation, *e.g.*, 2.504(7) means 2.504 ± 0.007 Å.

water molecules form hydrogen bonds among themselves and to polyanion oxygens. The intersheet linkages and the hydrogen bonds are shown in Figure 1, and the distances are given in Tables 13 (Sr–O) and 14 (hydrogen bonding and water molecule environment). The hydrogen bonds have been selected within the range of distances from 2.5 to 3.1 Å, avoiding edges of cation polyhedra. The shortest hydrogen bonds are those involving hydroxyls in the intersheet linkages. Only in a few cases is it possible to identify the atom donating its proton to form the bond (Table 14). In general, the bonding is among hydroxyls and water molecules and attempts to derive a donor scheme end in ambiguity. The presence of the heavy Sr atom prevents direct determination of proton

TABLE 14. HYDROGEN BONDS AND WATER MOLECULE ENVIRONMENT IN STRONTIOGINORITE (see Fig. 1)

Bond (Donor marked by *)	Coordinates of second atom[a]			Bond length (Å)	Bond (Donor marked by *)	Coordinates of second atom[a]			Bond length (Å)
	x	y	z			x	y	z	
Hydroxyl ions					*Water molecules*				
OH(8)–OH(24)*	0.4048	−0.1170	−0.2329	2.691(9)[b]	H₂O(3)–OH(9)	0.3876	0.3922	1.0146	2.70(1)[b]
OH(8)*–OH(9)	.1124	.1078	.0146	2.923(9)	H₂O(3)–H₂O(2)	.3463	.5614	.7286	2.79(1)
OH(9)–H₂O(3)	.2367	.4502	.1507	2.70(1)	H₂O(3)*–O(4)	.2426	.5967	1.0046	2.893(9)
OH(9)–H₂O(4)	.4833	.5384	.1339	2.75(1)	H₂O(3)–Sr	.1178	.3289	.7364	2.570(7)
OH(9)–H₂O(4)	.5167	.4616	.1339	2.93(1)					
OH(9)–OH(8)*	.2077	.4625	.1003	2.923(9)			Angles (°)		
OH(19)–H₂O(1)*	.3904	.6489	.2793	2.76(1)	OH(9)–H₂O(3)–Sr	104.5(3)	OH(9)–H₂O(3)–H₂O(2)		118.8(3)
OH(19)*–O(20)	.1190	.6160	.5102	2.814(9)	H₂O(2)–H₂O(3)–Sr	76.9(3)	OH(9)–H₂O(3)–O(4)		112.9(3)
OH(21)*–O(15)	.2651	.0929	.5243	2.618(8)	O(4)–H₂O(3)–Sr	90.6(3)	H₂O(2)–H₂O(3)–O(4)		144.7(3)
OH(23)*–O(5)	.6355	.1038	.1369	2.595(9)					
OH(24)*–OH(8)	.7077	.0375	.1003	2.691(9)	H₂O(4)–OH(9)	.1124	−0.1078	0.9854	2.75(1)
					H₂O(4)–H₂O(1)	.1096	.1489	.7207	2.88(1)
Water molecules					H₂O(4)–H₂O(2)	−.1537	−.0614	.7285	2.90(1)
H₂O(1)*–OH(19)	.2293	.0488	.6028	2.76(1)	H₂O(4)–OH(9)'	.1124	.1078	1.0146	2.93(1)
H₂O(1)–H₂O(4)	.0167	.0384	.8661	2.88(1)					
H₂O(1)–H₂O(5)	−.0509	.0246	.5992	2.93(1)			Angles (°)		
H₂O(1)–Sr	.1178	.3289	.7364	2.608(7)	OH(9)–H₂O(4)–H₂O(1)	126.0(3)	H₂O(1)–H₂O(4)–H₂O(2)		104.0(3)
					OH(9)–H₂O(4)–H₂O(2)	98.9(3)	H₂O(1)–H₂O(4)–OH(9)'		125.9(3)
	Angles (°)				OH(9)–H₂O(4)–OH(9)'	98.7(3)	H₂O(2)–H₂O(4)–OH(9)'		96.2(3)
OH(19)–H₂O(1)–H₂O(4)	114.0(3)	OH(19)–H₂O(1)–Sr		123.1(3)					
OH(19)–H₂O(1)–H₂O(5)	78.3(3)	H₂O(4)–H₂O(1)–Sr		121.2(3)	H₂O(5)–H₂O(2)	0.1537	0.0614	0.2715	2.62(1)
H₂O(4)–H₂O(1)–H₂O(5)	70.5(3)	H₂O(5)–H₂O(1)–Sr		131.7(3)	H₂O(5)*–O(16)	−.1320	.0826	.3694	2.77(1)
					H₂O(5)–H₂O(1)	−.1096	−.1489	.2793	2.93(1)
H₂O(2)–H₂O(5)	0.0509	−0.0246	0.4008	2.62(1)					
H₂O(2)–H₂O(3)	.2633	.0498	.1507	2.79(1)			Angles (°)		
H₂O(2)–H₂O(4)	−.0167	.0384	.1339	2.90(1)	H₂O(2)–H₂O(5)–O(16)	99.2(3)	O(16)–H₂O(5)–H₂O(1)		77.3(3)
H₂O(2)–Ca	.1264	.2187	.2463	2.313(8)	H₂O(2)–H₂O(5)–H₂O(1)	110.1(3)			
	Angles (°)								
H₂O(5)–H₂O(2)–H₂O(3)	116.5(3)	H₂O(5)–H₂O(2)–Ca		118.2(3)					
H₂O(5)–H₂O(2)–H₂O(4)	74.6(3)	H₂O(3)–H₂O(2)–Ca		124.6(3)					
H₂O(3)–H₂O(2)–H₂O(4)	77.3(3)	H₂O(4)–H₂O(2)–Ca		109.2(3)					

a For each of the bonds listed the coordinates of the first atom are given in Table 3.
b Errors are given in parentheses and correspond to one standard deviation, e.g. 2.691(9) means 2.691 ± 0.009 Å.

Table 15. Charge Balance for Oxygen and Hydroxyl Ions in Strontiginoriote

Oxygen or hydroxyl ion	Contribution in valence units[a]			H–bond	Σ	Oxygen or hydroxyl ion	Contribution in valence units[a]			H–bond	Σ
	B	Ca	Sr	bond	Σ		B	Ca	Sr	bond	Σ
Polyanion I						Polyanion II					
O(1)	1.92	—	—	—	1.92	O(12)	1.96	—	—	—	1.96
O(2)	1.76	0.25	—	—	2.01	O(13)	1.79	—	0.20	—	1.99
O(3)	1.88	0.25	—	—	2.13	O(14)	1.79	—	0.20	—	1.99
O(4)	1.83	—	—	0.17	2.00	O(15)	1.79	—	—	0.29	2.08
O(5)	1.87	—	—	0.30	2.17	O(16)	1.83	—	—	0.22	2.05
O(6)	1.79	—	0.20	—	1.99	O(17)	1.78	0.25	—	—	2.03
O(7)	1.81	0.25	—	—	2.06	O(18)	1.78	—	0.20	—	1.98
OH(8)	0.93	—	—	1.09	2.02	OH(19)	1.01	—	—	1.02	2.03
OH(9)	0.81	—	—	1.29	2.10	O(20)	1.82	—	—	0.20	2.02
O(10)	1.36	—	0.20	—	2.06	O(25)	1.76	0.25	—	—	2.01
O(11)	1.79	0.25	—	—	2.04	O(26)	1.80	—	0.20	—	2.00
						Side chain					
						OH(21)	0.98	—	0.20	0.70	1.88
						O(22)	1.96	—	—	—	1.96
						OH(23)	1.03	—	0.20	0.70	1.93
						OH(24)	0.97	0.25	—	0.75	1.97

[a] Assigned as follows: B and H–bond contributions from relationships with B–O and H–bond lengths as given by Zachariasen (1963); Ca and Sr contributions $2/8 = 0.25$ and $2/10 = 0.20$, respectively.

positions, which were sought but not found in the final difference Fourier.

Charge Balance Considerations. In Table 15, the charge contributions of boron, Ca, and Sr to each oxygen or hydroxyl ion of the polyanion are given. In assigning the boron contribution, the B–O distance was taken into account, following the bond length-bond strength relationship given by Zachariasen (1963). Cation-oxygen distances were not taken into account for the Sr and Ca contributions, each Sr–O bond being assigned a value of $2/10 = 0.20$ valence units, and each Ca–O bond a value of $2/8 = 0.25$ v.u. The calculated sums for the contributions of boron, Sr, and Ca deviate considerably from the expected values of 2 v.u. for an oxygen ion and 1 v.u. for a hydroxyl ion. However, when the hydrogen bonds are considered, again following a method proposed by Zachariasen (1963), the sum for each oxygen, taken over all 26 oxygens of the sheet, averages to 2.02 v.u. Considering the difficulties in assignment of proton donors in strontioginorite, the calculated value of the charge balance for each oxygen is satisfactory (Table 15). Moreover, it is clear that hydrogen bonds do occur (Table 14) where the deficiencies found on the simpler model would indicate.

Reyershausen crystals, which he initially received through the courtesy of the late Dr. Otto Braitsch, University of Göttingen. Mr. Erd also participated in numerous helpful discussions. H. J. Rose, Jr., and Ralph Christian carried out the X-ray fluorescence analysis. Daniel E. Appleman provided material assistance with computer problems and also valuable discussion including critical review of the manuscript. M. Fleischer has continually furnished us with English translations from the Russian literature on borates. We are also grateful to Dr. L. W. Finger of the Geophysical Laboratory for the use of various computer programs written by him, and for much helpful discussion concerning their use.

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