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SIGISMUNDITE, $(Ba,K,Pb)Na_3(Ca,Sr)(Fe,Mg,Mn)_{14}Al(OH)_2(PO_4)_{12}$, A NEW Ba-RICH MEMBER OF THE ARROJADITE GROUP FROM SPLUGA VALLEY, ITALY

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ABSTRACT

The new mineral species sigismundite $(Ba,K,Pb)Na_3(Ca,Sr)(Fe,Mg,Mn)_{14}Al(OH)_2(PO_4)_{12}$, a Ba-rich member of the arrojadite family, occurs as greyish green lumps in phengitic quartzite at Madesimo, Spluga Valley, Italy, associated with quartz, apatite, and lazulite. Sigismundite is monoclinic, space group *C*2/*c*, with *a* 16,406(5), *b* 9.945(3), *c* 24.470(5) Å, β 105.73(2)°, D_x 3.544 g/cm³, $n_{(average)}$ 1.65(1). The structure has been refined using 2846 observed reflections $[I > 3\sigma(I)]$ down to $R = 0.066$. This mineral differs from arrojadite by the replacement of K by Ba, the presence of considerable content of Mg in place of transition metals, and vacancies in the Na site. The strongest lines in the powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 3.010(100)$(42\bar{4})$, 3.178(51)(206), 2.678(42)(226), 2.523(27)$(60\bar{6})$, 2.805(25)$(31\bar{8})$, 4.519(23)(114), 2.775(21)(134), 2.741(21)$(13\bar{5})$, and 2.732(21)$(60\bar{2})$.

Keywords: sigismundite, new mineral species, barium analogue, arrojadite – dickinsonite series, X-ray data, crystal-structure refinement, Spluga Valley, Italy.

SOMMAIRE

La sigismundite, nouvelle espèce minérale de composition $(Ba,K,Pb)Na_3(Ca,Sr)(Fe,Mg,Mn)_{14}Al(OH)_2(PO_4)_{12}$, fait partie de la famille de l'arrojadite, dont c'est l'analogue baryfère. On la trouve en amas vert grisâtre dans une quartzite à phengite à Madesimo, vallée du Spluga, en Italie, en association avec quartz, apatite et lazulite. La sigismundite est monoclinique, groupe spatial *C*2/*c*, avec *a* 16.406(5), *b* 9.945(3), *c* 24.470(5) Å, β 105.73(2)°, D_x 3.544 g/cm³, $n_{(moyen)}$ 1.65(1). Nous en avons affiné la structure en utilisant 2846 réflexions observées $[I > 3\sigma(I)]$ jusqu'à un résidu *R* égal à 0.066. Elle se distingue de l'arrojadite par le remplacement de K par Ba, la présence d'une teneur importante en Mg à la place des métaux de transition, et des lacunes dans les sites occupés par le Na. Les raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont: 3.010(100)$(42\bar{4})$, 3.178(51)(206), 2.678(42)(226), 2.523(27)$(60\bar{6})$, 2.805(25)$(31\bar{8})$, 4.519(23)(114), 2.775(21)(134), 2.741(21)$(13\bar{5})$, et 2.732(21)$(60\bar{2})$.

(Traduit par la Rédaction)

Mots-clés: sigismundite, nouvelle espèce minérale, analogue baryfère, solution solide arrojadite – dickinsonite, données de diffraction X, affinement de la structure cristalline, vallée du Spluga, Italie.

INTRODUCTION

An interesting occurrence of phosphates was discovered recently near Madesimo, Spluga Valley, Central Alps, Italy. These phosphates include lazulite and apatite as the most abundant representatives, with minor amounts of svanbergite, woodhouseite, goyazite, and crandallite. Of these minerals, svanbergite and woodhouseite are particularly rare in the Alpine region, which emphasizes the importance of the locality (Guelfi & Orlandi 1987, Bedognè *et al.* 1995). A few years ago, Dr. Paolo Gentile, a mineral collector, gave us a grayish green lump of an unknown mineral, found in association with the other phosphates described above. Detailed examination confirmed the mineral to be a new Ba-rich member of the arrojadite – dickinsonite series; it is called sigismundite in honor of Pietro Sigismund (1874 – 1962), a well-known collector of minerals from Valtellina (especially Val Malenco). The new mineral and the mineral name have been approved by the IMA Commission on New Minerals and Mineral Names. The type material has been deposited at the Civic Museum of Natural History, Morbegno, Sondrio, Italy.

The very complex crystal-chemistry of the arrojadite – dickinsonite series has been the object of considerable investigation (Moore & Ito 1979, Moore *et al.* 1981, Merlino *et al.* 1981). To provide an easy comparison of the corresponding data in the discussion of the structure, the same labeling of the atomic positions used by these authors has been adopted here for sigismundite.

OCCURRENCE AND PARAGENESIS

A single specimen of sigismundite was found in phengitic quartzite at Madesimo, Spluga Valley, northern Italy. The Tambó and Suretta Upper Penninic nappes outcrop in the Spluga Valley; they dip slightly eastward and are formed by a pre-Permian basement consisting of paragneiss and micaceous schist, with layers of amphibolite and orthogneiss, and Variscan metagranitoid rocks. These nappes are separated by a Permo-Mesozoic metavolcanic and metasedimentary sequence, composed of metarhyolite, quartz schists and chloritic–phengitic gneiss (Permian), phengitic quartzite (Upper Permian to Lower Triassic), and of calcite and dolomite marbles, gypsum and carbonate breccias (Middle to Upper Triassic). The quartzite beds, derived from quartz-rich sandstones with conglomerate layers, were formed during Alpine metamorphism, and range from eclogite facies to blueschists facies, with a subsequent extensive retrogression to the greenschist facies. The presumable presence of organic matter in the sediments from which the sandstones originated gave rise to the formation of various phosphates embedded in the quartzites. These rocks contain abundant quartz, phengitic mica, chlorite, feldspars and rare accessory minerals (see below).

Sigismundite is associated with quartz, albite, apatite and ferrous carbonates partly transformed into iron oxides. Other primary metamorphic minerals in the phosphate-bearing quartzitic layers are K-feldspar, rutile, schorl, barite, celestite, lazulite, woodhouseite, goyazite and pyrophyllite. Secondary minerals derived from alteration of the above species are crandallite, kaolinite, mitridatite and diaspore. In the fissures and vugs of the quartzite, there are crystals of quartz, apatite, svanbergite, barite, hematite, vanadinite and rare orange-red woodhouseite (Bedognè *et al.* 1995). Although a number of similar outcrops of phosphate-bearing rocks occur in the vicinity (Val Scalcoggia, Dair in Bregaglia Valley), sigismundite was found at a single locality.

APPEARANCE AND PHYSICAL PROPERTIES

The only specimen of sigismundite that has been found so far consists of a small grayish green lump, up to 4 cm in size, somewhat similar to massive apatite, directly included in the rock. The mineral is brittle, the streak is white, and the luster is greasy. On inspecting a thin section of the lump with a petrographic microscope, a number of quartz grains are evident at the border, intermixed with flakes of a colorless phengite-like mica. The quartz grains are partly idiomorphic where they are in contact with sigismundite. The texture of accompanying minerals clearly indicates that the lump of sigismundite is a structural relic with respect to the last stage of deformation of the host rock. The individual crystals of sigismundite are imperfect, translucent, up to 1 cm across. These crystals are intensely microfractured, in some cases being almost completely divided into subindividuals (about 10 – 20 μm in size) slightly misoriented with respect to each other. Within the microfractures, quartz, apatite and an abundant carbonate similar to ankerite are invariably present, and replace a significant portion of sigismundite. Another distinct set of fractures formed at a later stage is also present throughout the sample; these fractures are almost perpendicular to the elongation of the sigismundite lump and are filled with a number of other minerals, which cannot be identified by optical means alone.

Within the lump, the original crystals of sigismundite show rather straight borders, and often give rise to a sort of pavement-like aggregations. In one case only, a crystal of comparatively regular form was noticed: its habit is elongate, and the crystal faces seem to be almost parallel to the elongation. Under polarized light, sigismundite shows a greenish yellow color, without appreciable pleochroism; no zoning was observed, so that extensive variation of the chemical composition is not expected, in agreement with the

TABLE 1. ANALYTICAL RESULTS FOR SIGISMUNDITE

	wt% **	range
P_2O_5	40.50	39.88 - 40.96
SiO_2	0.02	0.01 - 0.03
Al_2O_3	2.45	2.40 - 2.54
FeO	27.64	26.86 - 28.11
MgO	10.85	10.64 - 10.93
MnO	0.70	0.65 - 0.75
Na_2O	4.44	4.32 - 4.58
K_2O	0.26	0.25 - 0.28
BaO	5.68	5.61 - 5.85
PbO	0.76	0.63 - 0.89
CaO	2.09	2.00 - 2.20
SrO	1.09	0.99 - 1.30
$(H_2O)^*$	0.86	
Total	**97.34**	

EMPIRICAL FORMULA:
$(Ba_{0.78},K_{0.12},Pb_{0.07},Sr_{0.02})_{\Sigma=0.99}Na_{3.02}(Ca_{0.79},Sr_{0.20})_{\Sigma=0.99}$

$(Fe_{8.12}, Mg_{5.68},Mn_{0.21})_{\Sigma=14.01}Al_{1.01}(OH)_2(PO_4)_{12}$

SIMPLIFIED FORMULA:
$(Ba,K,Pb)Na_3(Ca,Sr)(Fe,Mg,Mn)_{14}Al(OH)_2(PO_4)_{12}$

* The water content has been deduced in agreement with the crystal structure data

**average of 10 determinations on an ARL-SEMQ electron microprobe

Conditions: Accelerating voltage 20 kV, sample current on brass 15 nA, ZAF correction program from TRACOR.

Analytical standards (natural standards): kaersutite Si, Al, Mg, Ca, K; spessartine Mn, Fe; apatite (USNM 104021, Jarosewich *et al.* 1980) P; celsian Ba; celestite Sr; anglesite Pb; albite Na.

results obtained with an electron microprobe (see Table 1, and below). The above-mentioned fractures seem to indicate the presence of two different cleavage planes, one more distinct than the other, making an angle of about 110°. The interference colors are very low, and can be roughly compared with those of the quartz crystals present in the same section. For the only distinct crystal observed (see above), the extinction angle is about 25° with respect to the elongation. Because of the presence of considerable extraneous material, and of the poor quality of the crystals, no clear interference figures could be obtained.

Owing to this inhomogeneity of the sample due to the presence of several phases in the microstructure, a reliable experimental value of density could not be obtained; the calculated value is 3.544 g/cm^3. No fluorescence at 254 nm and 366 nm was observed. Using a Rayner total-reflection refractometer, only an average index of refraction n [= 1.65(1)] could be measured; it compares very favorably with the corresponding n_{calc} (= 1.639) from the Gladstone–Dale rule. According to the criterion of Mandarino (1981), the compatibility index is superior (–0.011).

EXPERIMENTAL PROCEDURES

Chemical analysis

Electron-microprobe analysis was done on polished grain-mounts by using an ARL–SEMQ instrument of the Italian National Research Council (C.N.R.) at Centro di Studio per la Geodinamica Alpina e Quaternaria, Milan. The standards and operating conditions are reported in Table 1; no extensive variation in the composition was found in the different points examined, as shown in the third column of Table 1. An energy-dispersion analysis was also performed using a KEVEX Delta5 equipment attached to a S2700 Hitachi scanning electron microscope, which has proved to be particularly useful in detecting the lighter elements. By this method, in addition to the previous data, noticeable amounts of fluorine were observed, so that some substitution of the OH group [*O*(25)] by fluorine can be inferred, similarly to what is found in most minerals of the arrojadite group. The amount of water reported in Table 1 has been deduced from the results of crystal-structure refinement and is relative to the pure hydroxyl-rich end member.

X-ray-diffraction study

The X-ray powder-diffraction pattern, recorded using a Rigaku D/IIIMAX diffractometer (Ni-filtered Cu*K*α radiation, internal standard: quartz) is reported in Table 2. The calculated pattern was obtained using the program POWLS80 (Will 1979); the unit-cell parameters refined from these data are reported in Table 3. A comparison of Table 2 with the corresponding powder pattern for arrojadite (see, for instance, Table 10 in Moore *et al.* 1981) shows that the differences are minor, and mostly concern low-angle or weak reflections; for instance, the {002} reflection (in our *C*2/*c* setting) is missing for sigismundite and, conversely, the {110} reflection is missing for arrojadite. To determine the structure, a crystal measuring about 0.22 × 0.23 × 0.10 mm^3 was mounted on an Enraf–Nonius CAD4 diffractometer, and twenty-five intense reflections with $8.2 < \theta < 14.0°$ were centered using graphite-monochromated Mo*K*α radiation (λ = 0.71073 Å). The unit-cell parameters (Table 3) were obtained by refinement of their setting angles, together with an orientation matrix relating the crystal axes to the diffractometer axes. A total of 5747 diffracted intensities were collected at room temperature with variable scan-speed (maximum scan-time for each reflection: 90 s), for $-18 \leq h \leq 18$, $0 \leq k \leq 10$ and $0 \leq l \leq 25$, to a maximum 2θ angle of 60°. Reference reflections were periodically monitored during the data collection to assess instrument stability. The diffracted intensities were corrected for Lorentz, polarization and background effects.

TABLE 2. OBSERVED AND CALCULATED X-RAY POWDER DIFFRACTION DATA FOR SIGISMUNDITE

h	*k*	*l*	I/I_0	d_{obs}	d_{calc}	*h*	*k*	*l*	I/I_0	d_{obs}	d_{calc}
1	1	0	8	8.383	8.405	1	3	3	7	2.937	2.937
2	0	-2	5	7.528	7.572	5	1	-5	7	2.896	2.897
1	1	-2	7	7.339	7.360	3	3	-2	20	2.819	2.819
2	0	2	7	5.855	5.855	3	1	-8	25	2.805	2.807
2	0	-4	5	5.470	5.481	1	3	4	21	2.775	2.773
1	1	-4	6	5.185	5.182	1	3	-5	21	2.741	2.740
0	2	0	5	4.961	4.966	6	0	-2	21	2.732	2.729
3	1	-2	6	4.729	4.728	2	2	6	42	2.678	2.679
3	1	0	7	4.642	4.647	3	3	2	11	2.640	2.640
0	2	2	15	4.566	4.575	5	1	3	8	2.592	2.592
1	1	4	23	4.519	4.519	1	3	-6	13	2.570	2.568
2	2	0	7	4.199	4.202	6	0	-6	27	2.523	2.524
2	2	-2	15	4.155	4.153	0	4	0	13	2.486	2.483
3	1	2	8	3.998	4.005	1	3	-7	6	2.401	2.400
0	2	4	8	3.792	3.793	6	2	-2	8	2.393	2.392
3	1	-6	13	3.427	3.429	7	1	-6	12	2.180	2.179
1	1	6	20	3.368	3.369	0	2	10	9	2.125	2.125
3	1	4	16	3.279	3.282	2	2	10	12	1.935	1.936
2	2	4	12	3.202	3.206	0	4	8	19	1.897	1.897
2	0	6	51	3.178	3.181	8	2	2	14	1.744	1.745
3	1	-7	13	3.097	3.099	6	0	8	14	1.740	1.739
4	2	-4	100	3.010	3.011	2	6	2	14	1.592	1.593

An empirical absorption-correction was applied according to the procedure already described in Demartin *et al.* (1992); the minimum transmission factor is 0.61. After averaging the symmetry-related data (R_{sym}= 4.7% on F_o), 5401 independent reflections were obtained; of these, 2846 with $I > 3\sigma(I)$ were used for the structure refinement.

TABLE 3. CRYSTAL DATA FOR SIGISMUNDITE

	single crystal	powder data
a (Å)	16.406(5)	16.394(4)
b (Å)	9.945(3)	9.932(2)
c (Å)	24.470(5)	24.437(7)
β (°)	105.73(2)	105.78(2)
V (Å^3)	3843(2)	3828(1)

CRYSTAL SYSTEM: monoclinic SPACE GROUP: *C2/c* *Z*= 4

Measured reflections: 5747 with $4 < 2\theta < 60$ °

Independent observed reflections with $I > 3\sigma(I)$: 2846

R = 0.066 R_w = 0.073

$R = [\Sigma(Fo\text{-}k|Fc|)/\Sigma Fo]$; $R_w = [\Sigma w(Fo\text{-}k|Fc|)^2/\Sigma wFo^2]^{1/2}$

TABLE 4. FRACTIONAL ATOMIC COORDINATES FOR SIGISMUNDITE

Atom	Mult.	x	y	z	Beq/B(Å^2)
Al	1/2	0.000	0.500	0.000	0.51(7)
X(1)	0.583(7)	0.2299(3)	0.2192(4)	0.4832(2)	2.27(8)
X(2)	1	0.1345(5)	0.5171(5)	0.1206(3)	3.3(1)
X(3)	1/2	0.000	0.000	0.000	1.9(1)
X(4)	0.080(8)	0.000	0.014(4)	0.250	1.1(6)*
X(4x)	0.050(8)	0.000	0.116(6)	0.250	1.0(10)*
X(5)	0.485(2)	0.000	0.4990(1)	0.250	1.90(2)
M(1)	0.437(5)	0.2231(3)	0.8881(4)	0.4768(2)	1.31(7)
M(1x)	0.126(5)	0.205(1)	0.948(1)	0.4545(6)	1.7(3)
M(2)	0.840(5)	0.2118(1)	0.0138(2)	0.26768(8)	0.99(3)
M(3)	0.512(4)	0.1071(2)	0.0165(3)	0.1404(1)	0.85(5)
M(4)	0.687(5)	0.0215(2)	0.2509(2)	0.4023(1)	0.99(4)
M(5)	0.893(4)	0.0338(1)	0.7449(2)	0.40019(8)	0.86(3)
M(6)	0.895(5)	0.2036(1)	0.7014(2)	0.35236(8)	1.08(3)
M(7)	0.785(5)	0.2180(1)	0.2930(2)	0.3432(1)	1.31(4)
P(1)	0.620(8)	0.1156(3)	0.0109(4)	0.3689(2)	0.80(7)
P(1x)	0.380(8)	0.0802(4)	0.0005(7)	0.3349(3)	0.9(1)
P(2)		0.1299(2)	0.4648(2)	0.4234(1)	0.78(5)
P(3)		0.1265(2)	0.2510(3)	0.0395(1)	0.66(4)
P(4)		0.1033(2)	0.7678(2)	0.0486(1)	0.67(5)
P(5)		0.1294(2)	0.7269(2)	0.2128(1)	0.66(5)
P(6)		0.1431(2)	0.3005(2)	0.2061(1)	0.75(5)
O(1)		0.0255(5)	0.0653(7)	0.3675(3)	1.2(1)
O(2)		0.1115(5)	-0.1389(7)	0.3630(3)	1.2(1)
O(3)		0.1480(5)	0.0808(8)	0.3245(4)	2.3(2)
O(4)	0.620	0.1808(8)	0.042(1)	0.4254(6)	1.5(2)*
O(4x)	0.380	0.023(2)	-0.036(2)	0.271(1)	1.9(4)*
O(5)		0.0500(5)	0.4412(6)	0.4443(3)	0.8(1)
O(6)		0.1199(5)	0.5963(7)	0.3901(4)	1.4(1)
O(7)		0.1289(5)	0.3424(7)	0.3851(3)	1.0(1)
O(8)		0.2096(6)	0.4608(9)	0.4716(4)	1.8(2)
O(9)		0.0841(5)	0.1684(7)	0.0768(3)	0.9(1)
O(10)		0.0959(5)	0.3968(7)	0.0369(3)	0.7(1)
O(11)		0.1076(5)	0.1883(7)	-0.0193(3)	0.8(1)
O(12)		0.2249(5)	0.2522(8)	0.0654(3)	1.3(1)
O(13)		0.0459(5)	0.6438(6)	0.0489(3)	0.7(1)
O(14)		0.0667(5)	0.8723(7)	0.0814(3)	0.9(1)
O(15)		0.0969(5)	0.8160(7)	-0.0109(3)	1.2(1)
O(16)		0.1950(5)	0.7326(8)	0.0778(4)	0.3(2)
O(17)		0.0474(5)	0.6742(7)	0.1719(3)	0.8(1)
O(18)		0.1324(5)	0.6760(7)	0.2718(3)	0.0(1)
O(19)		0.1330(6)	0.8816(7)	0.2108(4)	0.6(2)
O(20)		0.2050(5)	0.6707(7)	0.1941(3)	0.0(1)
O(21)		0.0589(5)	0.3476(7)	0.1663(4)	0.2(2)
O(22)		0.1490(6)	0.3545(8)	0.2654(4)	0.8(2)
O(23)		0.1493(5)	0.1461(7)	0.2058(3)	0.9(1)
O(24)		0.2178(6)	0.3579(7)	0.1856(4)	1.4(2)
O(25)†		0.2304(5)	-0.0024(8)	0.1389(3)	1.1(1)

† Atom labeled as F in Moore *et al.* (1981)
Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$Beq = 4/3[a^2ß(1,1)+b^2ß(2,2)+c^2ß(3,3)+ac(\cos b)ß(1,3)]$$

Scattering factors for neutral atoms and anomalous-dispersion corrections were taken from Cromer & Waber (1974) and Cromer (1974), respectively. Starting from the atomic positions reported in Moore *et al.* (1981), the structure was refined by full-matrix least-squares, by minimizing the function $\Sigma w(F_o - k|F_c|)^2$. The multiplicities of *X*(2), *X*(3), and Al sites did not show appreciable differences from 1.00, 0.50 and 0.50, respectively, and were fixed at these values during the subsequent cycles. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oLp$, $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics, k (= 0.04) is a coefficient for improving the goodness of fit, and *Lp* is the Lorentz-polarization factor. For all the calculations, we used the Personal SDP Structure Determination Package (Frenz 1988, 1991). The final *R* and R_w indices are 0.066 and 0.073, respectively; these values can be favorably compared with the best results reported in the literature

TABLE 5. BOND DISTANCES (Å) AND ANGLES (°) FOR SIGISMUNDITE

Al-O(5)a	× 2	1.866(5)
Al-O(10)	× 2	1.891(6)
Al-O(13)	× 2	1.885(6)
<Al-O>		1.881
M(1)-O(4)b		1.987(11)
M(1)-O(8)c		2.077(7)
M(1)-O(11)d		2.067(7)
M(1)-O(12)d		2.570(8)
M(1)-O(12)e		2.025(6)
<M(1)-O>		2.145
M(1x)-O(2)b		2.502(15)
M(1x)-O(8)c		2.163(15)
M(1x)-O(11)d		2.314(13)
M(1x)-O(12)e		2.379(14)
<M(1x)-O>		2.340
M(2)-O(3)		2.063(6)
M(2)-O(19)f		2.088(7)
M(2)-O(20)g		2.117(6)
M(2)-O(23)		2.058(6)
M(2)-O(24)g		2.081(6)
<M(2)-O>		2.081
M(3)-O(25)		2.042(6)
M(3)-O(1)a		2.186(7)
M(3)-O(9)		2.128(6)
M(3)-O(14)f		2.015(6)
M(3)-O(19)f		2.133(7)
M(3)-O(23)		2.025(6)
<M(3)-O>		2.088
X(1)-O(4)		2.264(11)
X(1)-O(7)		2.803(8)
X(1)-O(8)		2.433(7)
X(1)-O(8)h		2.195(8)
X(1)-O(15)d		2.253(7)
X(1)-O(15)g		2.901(8)
X(1)-O(16)d		2.576(8)
X(1)-O(16)g		2.183(7)
<X(1)-O>		2.451
X(2)-O(10)		2.307(7)
X(2)-O(13)		2.323(7)
X(2)-O(16)		2.690(7)
X(2)-O(17)		2.652(7)
X(2)-O(20)		2.404(8)
X(2)-O(21)		2.528(8)
X(2)-O(24)		2.393(8)
X(2).....O(12)		3.471(10)
<X(2)-O>		2.471

M(4)-O(1)		2.042(5)
M(4)-O(5)		2.142(5)
M(4)-O(7)		2.124(6)
M(4)-O(9)a		2.101(6)
M(4)-O(15)d		2.248(7)
M(4)-O(21)a		2.070(7)
<M(4)-O>		2.121
M(5)-O(2)b		2.102(6)
M(5)-O(6)		2.106(6)
M(5)-O(11)d		2.119(7)
M(5)-O(13)a		2.272(5)
M(5)-O(14)a		2.219(6)
M(5)-O(17)a		2.028(7)
<M(5)-O>		2.141
M(6)-O(25)e		2.281(6)
M(6)-O(2)b		2.254(6)
M(6)-O(6)		2.125(6)
M(6)-O(12)e		2.099(7)
M(6)-O(18)		2.016(7)
M(6)-O(24)e		2.366(6)
<M(6)-O>		2.190
M(7)-O(25)e		2.202(6)
M(7)-O(3)		2.386(7)
M(7)-O(7)		2.060(6)
M(7)-O(16)g		2.154(7)
M(7)-O(20)g		2.128(6)
M(7)-O(22)		2.027(8)
<M(7)-O>		2.160
X(3)-O(9)	× 2	2.615(6)
X(3)-O(11)	× 2	2.702(5)
X(3)-O(14)f	× 2	2.366(6)
X(3)-O(15)f	× 2	2.485(6)
<X(3)-O>		2.542
X(4)-O(1)	× 2	2.836(8)
X(4)-O(3)	× 2	2.694(11)
X(4)-O(19)f	× 2	2.926(15)
<X(4)-O>		2.819
X(4x)-O(1)	× 2	2.835(10)
X(4x)-O(3)	× 2	2.634(10)
X(4x)-O(23)	× 2	2.949(7)
<X(4x)-O>		2.806
X(5)-O(17)	× 2	2.846(6)
X(5)-O(18)	× 2	2.733(6)
X(5)-O(21)	× 2	2.909(6)
X(5)-O(22)	× 2	2.772(7)
<X(5)-O>		2.815

TABLE 5. — continued

P(1)-O(1)	1.566(7)
P(1)-O(2)	1.497(6)
P(1)-O(3)	1.503(7)
P(1)-O(4)	1.534(12)
<P(1)-O>	1.525
O(1)-P(1)-O(2)	108.9(4)
O(1)-P(1)-O(3)	110.0(4)
O(1)-P(1)-O(4)	111.9(5)
O(2)-P(1)-O(3)	114.0(4)
O(2)-P(1)-O(4)	107.0(5)
O(3)-P(1)-O(4)	105.1(5)
P(2)-O(5)	1.549(6)
P(2)-O(6)	1.526(6)
P(2)-O(7)	1.534(6)
P(2)-O(8)	1.505(8)
<P(2)-O>	1.529
O(5)-P(2)-O(6)	109.2(3)
O(5)-P(2)-O(7)	102.2(3)
O(5)-P(2)-O(8)	111.8(4)
O(6)-P(2)-O(7)	111.8(4)
O(6)-P(2)-O(8)	112.7(4)
O(7)-P(2)-O(8)	108.8(4)
P(4)-O(13)	1.552(6)
P(4)-O(14)	1.532(6)
P(4)-O(15)	1.510(7)
P(4)-O(16)	1.521(7)
<P(4)-O>	1.529
O(13)-P(4)-O(14)	102.3(3)
O(13)-P(4)-O(15)	111.9(4)
O(13)-P(4)-O(16)	109.8(3)
O(14)-P(4)-O(15)	110.9(3)
O(14)-P(4)-O(16)	112.8(4)
O(15)-P(4)-O(16)	109.1(4)
P(6)-O(21)	1.531(7)
P(6)-O(22)	1.527(7)
P(6)-O(23)	1.539(5)
P(6)-O(24)	1.552(7)
<P(6)-O>	1.537
O(21)-P(6)- O(22)	108.0(4)
O(21)-P(6)- O(23)	110.6(4)
O(21)-P(6)- O(24)	109.8(4)
O(22)-P(6)- O(23)	111.6(4)
O(22)-P(6)- O(24)	109.0(4)
O(23)-P(6)- O(24)	107.9(3)

P(1x)-O(1)	1.499(8)
P(1x)-O(2)	1.571(8)
P(1x)-O(3)	1.447(8)
P(1x)-O(4x)	1.633(20)
<P(1x)-O>	1.538
O(1)-P(1x)-O(2)	108.6(5)
O(1)-P(1x)-O(3)	117.2(5)
O(1)-P(1x)-O(4x)	109.5(8)
O(2)-P(1x)-O(3)	112.9(5)
O(2)-P(1x)-O(4x)	105.1(7)
O(3)-P(1x)-O(4x)	102.8(8)
P(3)-O(9)	1.528(6)
P(3)-O(10)	1.530(5)
P(3)-O(11)	1.522(6)
P(3)-O(12)	1.566(7)
<P(3)-O>	1.537
O(9)-P(3)-O(10)	109.7(3)
O(9)-P(3)-O(11)	109.6(3)
O(9)-P(3)-O(12)	110.5(4)
O(10)-P(3)-O(11)	111.6(3)
O(10)-P(3)-O(12)	107.4(3)
O(11)-P(3)-O(12)	108.0(3)
P(5)-O(17)	1.534(7)
P(5)-O(18)	1.520(6)
P(5)-O(19)	1.541(6)
P(5)-O(20)	1.539(6)
<P(5)-O>	1.534
O(17)-P(5)-O(18)	107.6(3)
O(17)-P(5)-O(19)	110.8(4)
O(17)-P(5)-O(20)	108.5(3)
O(18)-P(5)-O(19)	111.8(4)
O(18)-P(5)-O(20)	110.0(4)
O(19)-P(5)-O(20)	108.2(3)

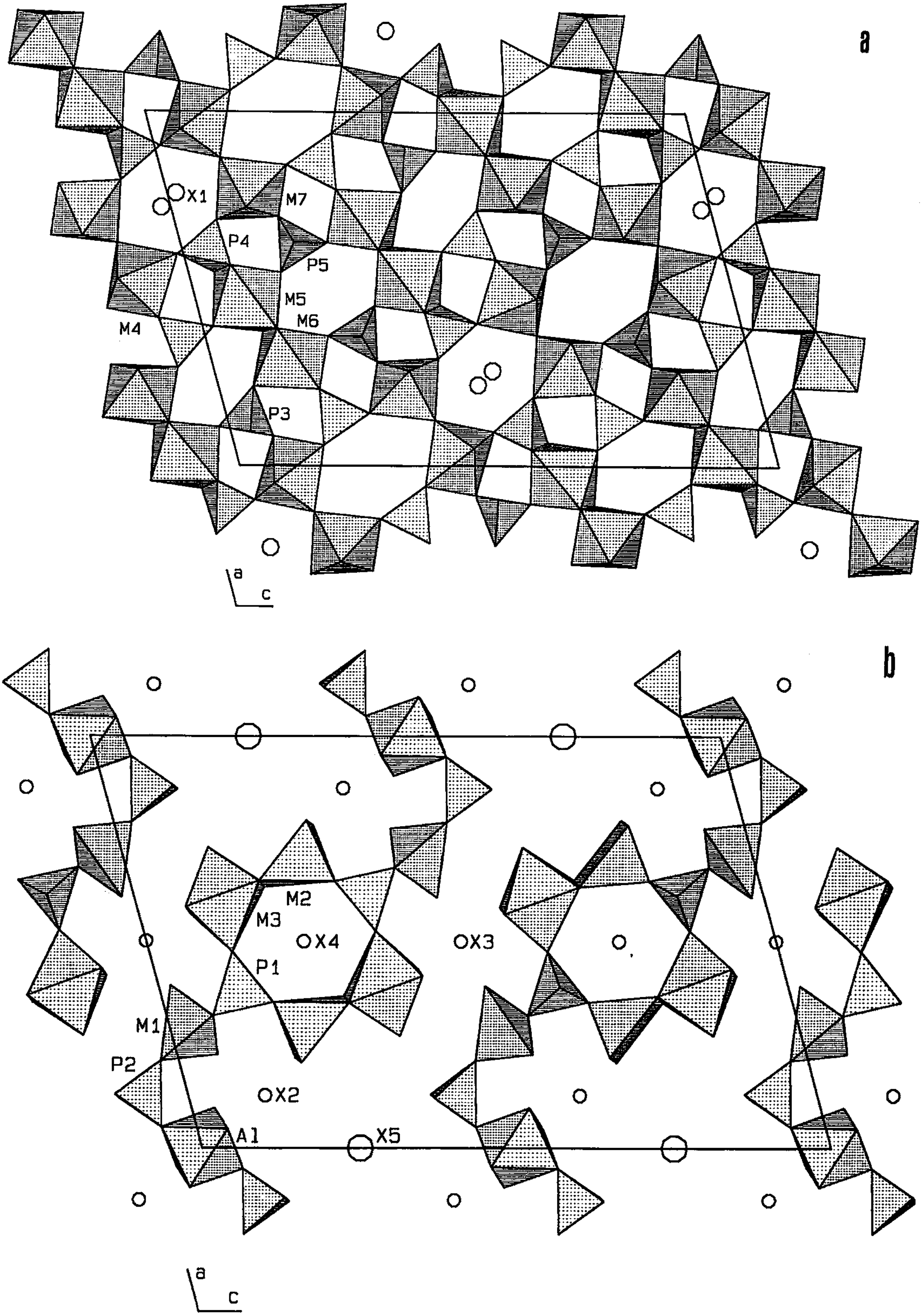
a = -x,y,1/2-z; b = x,1+y,z, c = 1/2-x, 3/2-y, 1-z;
d = x, 1-y, 1/2+z; e= 1/2-x, 1/2+y, 1/2-z; f = x, y-1, z;
g = 1/2-x, y-1/2, 1/2-z; h= 1/2-x, 1/2-y, 1-z.

for the other structures of the arrojadite group. Significant residuals of electron density in the final-difference Fourier synthesis [1.9(3) – 1.3(3) *e*/Å^3] are located close to the *X*(5) and *X*(4) positions, and indicate the presence of disorder. Final atomic coordinates are reported in Table 4, with bond distances and angles in Table 5. Tables of atomic displacement parameters and of observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Resarch Council, Ottawa, Ontario, Canada K1A 0S2. The atomic arrangement in two different planes at about $y = \frac{1}{4}$ and $y = \frac{1}{2}$ is shown in Figures 1a and 1b, respectively.

DISCUSSION

The structure refinement of sigismundite shows that the major differences with respect to the other minerals of the arrojadite – dickinsonite series are the replacement of K in the *X*(5) site by Ba and the presence of cation vacancies at the Na sites, the latter accounting for charge-balance requirements.

The existence of Ba-rich arrojadite has been known for a long time. A sample from the Buranga mine, Rwanda, contains 4.32 wt.% BaO, and another one from Sidi-Bou-Kricha, in Morocco, contains 5.36 wt.% BaO (Moore & Ito 1979). More recently, Robinson *et al.* (1992) described two samples of arrojadite from Rapid Creek, Yukon Territory, having a BaO content up to 7.00 wt.%; consequently, the possibility of existence of a new species, the barium analogue of arrojadite, was suggested. However, in sigismundite, a considerable amount of Mg also is present, exceeding the range of values so far reported for arrojadite – dickinsonite (Moore & Ito 1979, Robinson *et al.* 1992), and partly replacing transition metals at the *M* [*M*(1) to *M*(7)] sites. The *X*(1) site is half-occupied by Ca and Sr, and *X*(5) contains Ba and K. Since in arrojadite – dickinsonite, which is considerably richer in sodium


a
X1
M7
P4
P5
M5
M6
M4
P3
a
c
b
M2
M3
X4
X3
P1
M1
P2
X2
A1
X5
a
c

than sigismundite, Na occupies the sites $X(2)$, $X(3)$, $X(4)$, $X(6)$, and $X(7)$, a low occupancy of these sites was expected for sigismundite already on grounds of chemical analysis. The refinement of the crystal structure has indeed shown that in sigismundite, only the $X(2)$ and $X(3)$ sites are fully occupied by Na, whereas the $X(4)$ site is only partly occupied, and the $X(6)$ and $X(7)$ sites are empty.

The refinement of the multiplicity of the Al site shows that no significant replacement by other elements should occur; this result is in complete agreement with results of the chemical analysis.

Disorder of phosphate groups

Similar to arrojadite from Nickel Plate, South Dakota (Moore *et al.* 1981), one of the six non-equivalent PO$_4$ groups is disordered into two alternative orientations, centered on $P(1)$ and $P(1\text{x})$, with a $P(1)$–$P(1\text{x})$ distance of 0.882(7) Å. The model of disorder statistically consists of two face-sharing tetrahedra having the fourth vertex alternatively on opposite sides with respect to the shared face. A different situation was observed by Moore *et al.* (1981) in the structure of two other members of the family, where a common *edge* is shared between the two disordered tetrahedra.

The M sites

The seven cation sites $M(1)$ to $M(7)$ are essentially occupied by Fe^{2+}, Mg and Mn^{2+}. The refined multiplicity of these atomic positions (reported in Table 4) is based on the scattering curve of Fe. Unlike the members of the arrojadite – dickinsonite series, the quite peculiar $M(1)$ site is split into two sites $M(1)$ and $M(1\text{x})$, separated by 0.81(1) Å. The occupancy of the $M(1\text{x})$ position is correlated to the disorder involving the $P(1)$ phosphate group. Where the $M(1\text{x})$ site is occupied, then the alternative orientation of the phosphate group [with the $P(1\text{x})$ and $O(4\text{x})$ positions occupied] should occur, otherwise an $M(1\text{x})$–$O(4)$ distance of 1.18(2) Å would result. A similar steric effect couples the occupancy of $X(6)$ and $M(1)$ in arrojadite (Moore *et al.* 1981). In the present case, however, $X(6)$ is vacant. As in arrojadite – dickinsonite, the $M(2)$ polyhedron is a distorted square pyramid, and the $M(3)$, $M(4)$, $M(5)$ and $M(6)$ sites have distorted octahedral coordination. A slightly different situation can be observed for the $M(7)$ site: in arrojadite – dickinsonite, the $M(7)$ coordination polyhedron can be either a square pyramid or an octahedron (*i.e.*, disordered and partly occupied), with $O(4\text{x})$ included in the coordination sphere. In sigismundite, $M(7)$ is always octahedrally coordinated, with the $O(3)$ atom, which is not disordered, occupying the sixth position. The overall multiplicity of the M sites is 5.18 (on the basis of a Fe atomic scattering factor); the corresponding result from chemical analysis is 5.47. Because of the uncertainties in the multiplicity and because we have modeled the scattering factors to be of the same shape and proportional to the number of electrons, the result is considered acceptable.

The X sites

The X sites [$X(1)$ to $X(7)$] are occupied by large cations with a considerable range of ionic radius. The large values of the displacement parameters reflect the corresponding positional disorder. This is the reason why the largest residuals of electron density are close to these sites. $X(1)$ occurs close to an inversion center and is separated from its centrosymmetrical equivalent by 1.090(9) Å; thus it can be at most half-occupied. The geometry of this site corresponds to an 8-coordinated polyhedron with $X(1)$–O distances ranging from 2.183(7) to 2.901(8) Å. The site multiplicity (0.583) obtained by assuming the scattering factor of Ca for the atom in this position indicates that Ca is partly replaced by heavier cations. If all Ca and almost all Sr determined by chemical analysis are assigned to this site (Table 1), the calculated value of the site multiplicity [$0.5(Z_{\mathrm{Ca}}X_{\mathrm{Ca}} + Z_{\mathrm{Sr}}X_{\mathrm{Sr}})/Z_{\mathrm{Ca}} = 0.60$] is in good agreement with the refined value.

The $X(5)$–O distances (Table 5) are consistent with occupation of $X(5)$ by Ba, K, Pb^{2+} and Sr. Na occupies the $X(2)$ and $X(3)$ sites, and the $X(4)$ sites (see below) are only slightly populated by Na. The $X(6)$ and $X(7)$ sites of arrojadite – dickinsonite are vacant. Here, the scattering factor of Na has been assumed for $X(2)$ to $X(4)$, and that of Ba for $X(5)$.

In sigismundite, monovalent cations (*e.g.*, K) are extensively replaced by divalent cations (Ba and Pb^{2+}), and hence the structure should be deficient in some cations in order to maintain charge balance. This

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FIG. 1. The crystal structure of sigismundite, as seen along [010]: (a) part of the structure at about $y = ¼$; (b) part of the structure at about $y = ½$. The locations of the large cations [$X(1)$ to $X(5)$] are indicated by open circles; the other metal atoms are at the center of their coordination polyhedra [$M(1)$ to $M(7)$], and the phosphorus atoms [$P(1)$ to $P(5)$] are at the center of the tetrahedra.

explains the low content of Na in sigismundite, only about three-quarters of that found in most samples of arrojadite. If some cations are omitted from the structure [for instance, as a consequence of progressive oxidation or leaching of the mineral], the order of cation omission should be $X(6)$, $X(7) \cong X(4) > X(5) >> X(3)$ (Moore *et al.* 1981, p. 1043). This prediction is in good agreement with what is observed here, since the $X(6)$ and $X(7)$ sites are not occupied at all, and $X(4)$ is only sparsely populated. This latter site is split into two parts [$X(4)$ and $X(4\mathrm{x})$, separated by 1.00(5) Å], both involved in steric hindrance problems with the disordered phosphate group. These steric problems are particularly evident if one considers the following distances: $X(4)$–$O(4\mathrm{x})$ = 0.74(2) Å, $X(4\mathrm{x})$–$O(4\mathrm{x})$ = 1.60(4) Å; therefore, $X(4)$ and $X(4\mathrm{x})$ cannot both be populated if P is at $P(1\mathrm{x})$ and not $P(1)$.

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