Aravaite, $\text{Ba}_2\text{Ca}_{18}(\text{SiO}_4)_6(\text{PO}_4)_3(\text{CO}_3)\text{F}_3\text{O}$: modular structure and disorder of a new mineral with single and triple antiperovskite layers

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The crystal structure of the new mineral aravaite $\text{Ba}_2\text{Ca}_{18}(\text{SiO}_4)_6(\text{PO}_4)_3(\text{CO}_3)\text{F}_3\text{O}$ [$R\bar{3}m$, $a = 7.12550(11)$, $c = 66.2902(13)$ Å, $V = 2914.81(8)$ Å³, $Z = 3$] was solved from single-crystal diffraction data, collected using synchrotron radiation at the X06DA beamline of the Swiss Light Source. The unit cell of this modular mineral contains six layers of $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$ (T-layer), three triple antiperovskite layers (tAP) $\{(\text{F}_2\text{OCa}_{12})(\text{SiO}_4)_4\}^{4+}$, and three single antiperovskite layers (sAP) $\{(\text{FCa}_6)(\text{SiO}_4)_2\}^{3+}$. The structure refinement confirms a model with a layer sequence of T–sAP–T–tAP as an average structure of this mineral. However, one-dimensional diffuse scattering observed parallel to c^* implies imperfections in the stacking sequence of the average structure. Qualitative modelling of disorder confirms that the alternating sequence of T–sAP and T–tAP blocks is disturbed. The blocks occurring in this new mineral are known from other so-called hexagonal intercalated antiperovskite structures: T–sAP (stracherite and zadovite group), T–tAP (ariegilatite and nabimusaite group).

1. Introduction

Hexagonal antiperovskites are inorganic compounds built from units of anion-centred octahedra. Their structure can be considered as polytypic variations of the cubic perovskite structure, for example, as structures corresponding to the 2H, 4H and 9R polytypes reported by Gäbler & Niewa (2007). Many minerals can be described using antiperovskite units composed of face- and corner-sharing octahedra (Krivovichev, 2007, 2009). As they are not exclusively built from corner-sharing octahedra they are not considered as members of the perovskite supergroup (Mitchell *et al.*, 2017). Additionally, some minerals show antiperovskite modules, which are intercalated with intermediate ions and complexes (Krivovichev, 2007). The diversity of modular structures is well represented in the intercalated (or broken) antiperovskite minerals of the arctite supergroup (Galuskin *et al.*, 2018a). This supergroup combines silicate minerals of the nabimusaite group (Galuskin *et al.*, 2015a, 2018c; Galuskina *et al.*, 2018) and zadovite group (Galuskin *et al.*, 2015b, 2017, 2018b). The entire supergroup is characterized by modular structures containing single antiperovskite (sAP) layers of composition $\{[\text{WB}_6](\text{TO}_4)_2\}$, triple antiperovskite (tAP) layers $\{[\text{W}_3\text{B}_{12}](\text{TO}_4)_4\}$, and tetrahedral (T) layers $A(\text{TO}_4)_2$, where $A = \text{Ba}, \text{K}, \text{Sr} \dots$; $B = \text{Ca}, \text{Na} \dots$; $T = \text{Si}, \text{P}, \text{V}^{5+}, \text{S}^{6+}, \text{Al} \dots$; $W = \text{O}^{2-}, \text{F}^-$. The aforementioned

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layers are shown in Fig. 1. Minerals of the zadovite group contain sAP layers, whereas tAP layers are observed in minerals of the nabimusaite group. The units addressed as layers above may also be denoted as modules using the modular classification (Ferraris *et al.*, 2004).

Taking the chemical composition into account, we can describe the structure of the new intercalated antiperovskite mineral with alternating blocks of ariegilite $\text{BaCa}_{12}(\text{SiO}_4)_4(\text{PO}_4)_2\text{F}_2\text{O}$ (Galuskin *et al.*, 2018c) and stracherite $\text{BaCa}_6(\text{SiO}_4)_2[(\text{PO}_4)(\text{CO}_3)]\text{F}$ (Galuskin *et al.*, 2018b). These two minerals belong to the nabimusaite and zadovite groups, respectively. All of the mentioned structures show *R*-centred trigonal unit cells. Nabimusaite-group minerals with a sequence of T-tAP (3×) have a lattice parameter *c* of roughly 41 Å. The sequence T-sAP (3×) as found in zadovite-group minerals sums up to *c* ≈ 26 Å. The larger *c* parameter of circa 66 Å observed in aravaite is the sum of the sequence T-sAP-T-tAP (3×).

2. Occurrence

Aravaite (IMA 2018-078) was found in pyrometamorphic spurrite rocks of the Hatrurim Complex in the Negev Desert (31°13'58" N, 35°16'2" E) near Arad, Israel. These pyrometamorphic rocks are represented by spurrite marbles, larnite pseudo-conglomerates, gehlenite hornfelses and different paralavas, occurring widely along the rift zone of the Dead Sea (Bentor, 1960; Gross, 1977; Vapnik *et al.*, 2007; Sokol *et al.*, 2008; Galuskina *et al.*, 2014). Associated minerals are spurrite, calcite, brownmillerite, shulamite, CO_3 -bearing fluorapatite, brucite, fluor-mayenite-fluorkyuygenite, periclase, barytocalcite and baryte. Moreover, in the same rock samples, two other new minerals with antiperovskite modules were found: stracherite, $\text{BaCa}_6(\text{SiO}_4)_2[(\text{PO}_4)(\text{CO}_3)]\text{F}$, a mineral with single antiperovskite (sAP) layers (Galuskin *et*

Figure 1
The structure of aravaite consisting of blocks of ariegilite and stracherite. The structure is formed by ordered intercalation of T-modules = $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$ with antiperovskite layers of two types: tAP (triple antiperovskite module) = $\{(\text{F}_2\text{OCa}_{12})(\text{SiO}_4)_4\}^{4+}$ and sAP = $\{(\text{FCa}_6)(\text{SiO}_4)_2\}^{3+}$ (single antiperovskite module) in the sequence of T-sAP-T-tAP...

Figure 2
SEM micrographs (backscattered electron mode). (a) Aravaite intergrown with stracherite. A fragment of this crystal was used for the structural study. This is a rare example of spurrite marble, in which ariegilite is absent. (b) Epitaxial intergrowth of three intercalated antiperovskites: aravaite, ariegilite and stracherite. Arv is aravaite, Ari is ariegilite, HSi is undiagnosed hydrosilicates, May is fluormayenite-fluorkyuygenite, Shl is shulamite, Spu is spurrite, Sta is stracherite.

Table 1
Chemical composition as averaged from 41 (aravaite), 42 (stracherite) and eight (ariegilatite) spot measurements.
Note, that T1 and T2 denote the total of tetrahedral sites in the antiperovskite- and in the T-layers, respectively.

Wt %	Aravaite			Stracherite			Ariegilatite		
	Average	E.s.d.	Range	Average	E.s.d.	Range	Average	E.s.d.	Range
SO ₃	0.98	0.17	0.57–1.18	1.93	0.10	1.69–2.14	0.26	0.09	0.13–0.38
V ₂ O ₅	0.21	0.09	0.06–0.43	n.d.					
P ₂ O ₅	9.37	0.39	8.59–10.29	11.15	0.37	10.01–11.72	9.13	0.56	8.18–9.76
TiO ₂	0.13	0.05	0.06–0.26	n.d.			0.23	0.05	0.14–0.31
SiO ₂	18.61	0.29	18.07–19.22	15.14	0.15	14.89–15.45	19.55	0.35	18.99–19.98
Al ₂ O ₃	0.10	0.03	0.05–0.18	0.09	0.02	0.04–0.13	0.14	0.03	0.09–0.19
BaO	14.63	0.45	13.58–15.60	19.84	0.23	19.19–20.23	12.67	0.14	12.40–12.92
MnO	0.17	0.08	0–0.34	n.d.			0.18	0.07	0.08–0.31
CaO	50.88	0.59	49.65–52.43	45.46	0.17	45.07–45.74	54.23	0.43	53.80–55.03
MgO	0.10	0.08	0.04–0.56	n.d.					
K ₂ O	0.04	0.01	0–0.07	0.12	0.02	0.08–0.17			
Na ₂ O	0.46	0.12	0.18–0.93	0.05	0.02	0–0.11	0.25	0.08	0.17–0.45
CO ₂	2.30			4.60			1.15		
F	3.30	0.13	3.00–3.62	2.46	0.09	2.20–2.63	2.89	0.08	3.20–3.47
–O=F	1.39				1.04		1.41		
Total	99.90				99.80		99.48		
Ba	1.86			0.96			1.01		
K	0.02			0.02					
Na	0.12			0.01					
A	2.00			1.99			1.01		
Ca	17.73			6.01			11.86		
Na	0.17						0.10		
Mn ²⁺	0.05						0.03		
Mg	0.05								
B	18.00			6.01			12.99		
(SiO ₄) ^{4–}	5.93			1.87			3.92		
(AlO ₄) ^{5–}	0.04			0.01			0.03		
(TiO ₄) ^{4–}	0.03						0.04		
(PO ₄) ^{3–}				0.12			0.01		
T1	6.00			2.00			4.00		
(PO ₄) ^{3–}	2.58			1.04			1.57		
(CO ₃) ^{2–}	1.02			0.78			0.32		
(SO ₄) ^{2–}	0.24			0.18			0.04		
(SiO ₄) ^{4–}	0.12						0.07		
(VO ₄) ^{3–}	0.04								
T2	4.00			2.00			2.00		
F	3.23			0.96			1.87		
O	0.77			0.04			1.16		
W	4.00			1.00			3.03		

The empirical formulas are calculated on the basis of 30 (aravaite), 11 (stracherite) and 19 (ariegilatite) cations pfu and CO₂ by charge balance: (1) (Ba_{1.86}K_{0.02}Na_{0.12})Σ₂–(Ca_{17.73}Na_{0.17}Mg_{0.05}Mn²⁺_{0.05})Σ₁₈[(SiO₄)_{6.05}(PO₄)_{2.58}(CO₃)_{1.02}(SO₄)_{0.24}(AlO₄)_{0.04}(TiO₄)_{0.03}(VO₄)_{0.04}]Σ₁₀(F_{3.23}O_{0.77})Σ₄, (2) (Ba_{0.96}K_{0.02}Na_{0.01})Σ_{0.99}Ca_{6.01}[(SiO₄)_{1.87}(PO₄)_{0.12}(AlO₄)_{0.01}]Σ₂–[(PO₄)_{1.04}(CO₃)_{0.78}(SO₄)_{0.18}]Σ₂(F_{0.96}O_{0.04})Σ₁ and (3) Ba_{1.01}(Ca_{11.86}Na_{0.10}Mn²⁺_{0.03})Σ_{11.99}[(SiO₄)_{3.92}(PO₄)_{0.01}(AlO₄)_{0.03}(TiO₄)_{0.04}]Σ₄[(PO₄)_{1.57}(CO₃)_{0.32}(SO₄)_{0.04}V_{0.07}]Σ₂(F_{1.87}O_{1.16})Σ_{3.03}.

al., 2018*b*), and ariegilatite, BaCa₁₂(SiO₄)₄(PO₄)₂F₂O, with triple antiperovskite (tAP) layers (Galuskin *et al.*, 2018*c*). Rare grains of aravaite were detected as epitaxial intergrowth with stracherite or/and ariegilatite crystals [Figs. 2(*a*) and 2(*b*)]. Further details on the occurrence of these minerals are given by Galuskin *et al.* (2018*b,c*).

3. Methods of investigation

The morphology and chemical composition of aravaite and associated minerals were studied using optical microscopy, a scanning electron microscope Phenom XL, an electron

microprobe analyser and a micro-Raman spectrometer. The crystal structure was solved from synchrotron diffraction data.

3.1. Chemical analysis

Quantitative chemical analyses were performed using a CAMECA SX100 microprobe analyser (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland) at 15 kV and 10 nA, using the following lines and standards: Ba *Lα*, S *Kα*-baryte; P *Kα*-apatite; Ca *Kα*-wollastonite; Mg *Kα*, Si *Kα*-diopside; Fe *Kα*-hematite, Al *Kα*, K *Kα*-orthoclase; Ti *Kα*-rutile; Na *Kα*-albite, Sr *Lα*-SrTiO₃ and F *Kα*-fluorophlogopite. Results are given in Table 1.

3.2. Raman spectroscopy

Raman spectra of the new mineral aravaite, stracherite and ariegilatite were recorded on a WITec alpha 300R Confocal Raman Microscope (Department of Earth Science, University of Silesia, Sosnowiec, Poland) equipped with an air-cooled solid-state laser (532 nm) and a CCD camera operating at -61°C . The laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of 3.5 μm . An air Zeiss LD EC Epiplan-Neofluar DIC-100/0.75NA objective was used. Raman-scattered light was focused on a broad-band single-mode fibre with an effective pinhole size of about 30 μm . A monochromator with a 600 mm^{-1} grating was used. The power of the laser at the sample position was ~ 40 mW. An integration time of 5 s, with an accumulation of 15–20 scans and a resolution of 3 cm^{-1} were chosen. A standard measurement was performed using the Raman scattering line of a silicon plate (520.7 cm^{-1}). Fitting of spectra was performed with the help of the GRAMS/AI (Thermo Fisher Scientific) program using the mixed Lorentz–Gauss function.

3.3. Structural analysis

Single-crystal synchrotron radiation diffraction experiments were performed at the X06DA beamline at the Swiss Light Source (Paul Scherrer Institute, Villigen, Switzerland). The beamline is equipped with a multi-axis goniometer PRIGO (Waltersperger *et al.*, 2015) and a PILATUS 2M-F detector. Diffraction experiments were performed at ambient conditions using the DA+ (Wojdyla *et al.*, 2018) acquisition software. The radiation source is a SLS super-bending magnet (2.9 T). A wavelength of $\lambda = 0.70848$ Å is obtained using a Bartels monochromator. The detector was placed 120 mm from the sample, with a vertical offset of 67 mm, resulting in a maximum resolution of 0.7 Å. A total of 1800 frames were recorded using a fine-sliced (0.1°) ω -scan at 0.1 seconds per frame (crystal A). Experimental details are given in Table 2. Lattice parameters were determined using *CrysAlisPro* (Rigaku, 2016); the data reduction was processed with *XDS* (Kabsch, 2010). The original images of the diffraction data collection show evidence of one-dimensional diffuse scattering. Two further crystals (B, C) with different intensity patterns on the diffuse lines were re-measured to collect diffuse scattering data. These experiments were also performed at the SLS (beamline X06DA); however, this time an Aerotech one-circle goniometer was used. The detector was moved to a distance of 80 mm (with no vertical offset) and an exposure time of 0.6 s was used for each frame of 0.1° ω -rotation. To further investigate the distribution and orientation of the diffuse intensities within the reciprocal space, the orienting matrix was determined using *XDS* (Kabsch, 2010), and subsequently layers of the reciprocal space were reconstructed using a modified version of *Xcavate* (Estermann & Steurer, 1998). Line profiles were extracted from the reconstructed layers with *ImageJ* (Schneider *et al.*, 2012).

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{0.919}\text{Ba}_2\text{Ca}_{17.621}\text{F}_{3.462}\text{Na}_{0.379}\text{O}_{39.7}\text{P}_{2.96}\text{Si}_6$
M_r	1961.8
Crystal system, space group	Trigonal, $R\bar{3}m$
Temperature (K)	293
a, c (Å)	7.12550 (11), 66.2902 (13)
V (Å ³)	2914.81 (8)
Z	3
Radiation type, wavelength (Å)	Synchrotron, $\lambda = 0.70848$
μ (mm ⁻¹)	4.701
Crystal size (mm)	$0.06 \times 0.03 \times 0.03$
Data collection	
Diffractometer	Pilatus 2M-F
Absorption correction	Empirical (using intensity measurements)
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	5677, 1291, 1145
R_{int}	0.049
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.749
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.082, 0.183, 3.60
No. of reflections	1291
No. of parameters	85
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	12.08, -2.45

4. Results

4.1. Morphology and composition of the new antiperovskite

Results of chemical analyses (Table 1) and Raman spectroscopy (Fig. 3) show that the minerals stracherite, ariegilatite and aravaite are closely related. All three minerals can be seen together in a backscattered electron (BSE) image of spurrite marble (Fig. 2b). The morphology of the aggregates indicates oriented, *i.e.* epitaxial, intergrowth. Aravaite appears brighter than ariegilatite and darker than stracherite. It crystallizes after ariegilatite and is often overgrown later by stracherite (Fig. 2b). The new antiperovskite exhibits an homogeneous chemical composition and the content of main oxides shows values between stracherite and ariegilatite (Table 1). Its empirical formula is $(\text{Ba}_{1.86}\text{K}_{0.02}\text{Na}_{0.12})_{\Sigma 2}(\text{Ca}_{17.73}\text{Na}_{0.17}\text{Mg}_{0.05}\text{Mn}^{2+}_{0.05})_{\Sigma 18}[(\text{SiO}_4)_{6.05}(\text{PO}_4)_{2.58}(\text{CO}_3)_{1.02}(\text{SO}_4)_{0.24}(\text{AlO}_4)_{0.04}(\text{TiO}_4)_{0.03}(\text{VO}_4)_{0.04}]_{\Sigma 10}(\text{F}_{3.23}\text{O}_{0.77})_{\Sigma 4}$ and this can be simplified to $\text{Ba}_2\text{Ca}_{18}[(\text{SiO}_4)_6(\text{PO}_4)_3(\text{CO}_3)]\text{F}_3\text{O}$.

The Raman spectrum of aravaite is similar to spectra of ariegilatite and stracherite (Fig. 3). This is well recognizable from the example of the symmetric stretching ν_1 vibrations in $(\text{SiO}_4)^{4-}$. In the Raman spectrum of aravaite, three main bands are distinguished: 829, 852 and 877 (cm^{-1}). The first and third bands have analogues in the spectrum of ariegilatite and the second band (852 cm^{-1}) corresponds to the 859 cm^{-1} band in the stracherite spectrum. Consequently, it is reasonable to assume the presence of the two types of antiperovskite layer (tAP and sAP) in the structure of the new mineral. In the spectrum of aravaite, as well as in the stracherite spectrum, there is a strong band related to stretching vibrations of ν_1

Table 3
Atomic coordinates of aravaite.

Atom site	Atom type	Occu- pation	x	y	z	<i>U</i> _{iso}
Ba1	Ba	1	0	0	0.270337 (10)	0.0140 (3)
Ca1	Ca	1	0.49749 (8)	0.99499 (16)	0.23253 (2)	0.0066 (4)
Ca2	Ca	1	0.98845 (19)	0.49422 (9)	0.30918 (2)	0.0086 (4)
Ca3	Ca	0.937 (12)	0.48954 (9)	0.97909 (18)	0.146883 (19)	0.0058 (4)
Na3	Na	0.063 (12)	0.48954 (9)	0.97909 (18)	0.146883 (19)	0.0058 (4)
T1	Si	1	0.6667	0.3333	0.19130 (4)	0.0022 (5)
T2	Si	1	0.3333	0.6667	0.34596 (4)	0.0015 (5)
T3	Si	1	0	0	0.21838 (4)	0.0022 (5)
T4	P	0.940 (12)	0.6667	0.3333	0.26572 (5)	0.0063 (8)
T5p	P	0.54 (2)	0.3333	0.6667	0.27450 (7)	0.0071 (13)
T5c	C	0.46 (2)	0.3333	0.6667	0.27450 (7)	0.0071 (13)
O1	O	0.865 (14)	0.2223 (4)	0.7777 (4)	0.28273 (8)	0.017 (2)
O2	O	1	0.3333	0.6667	0.25243 (12)	0.012 (2)
O3	O	1	0.4578 (4)	0.9155 (7)	0.35310 (8)	0.0193 (16)
O4	O	1	0.6667	0.3333	0.28903 (12)	0.0103 (19)
O5	O	1	0.5421 (3)	0.0842 (7)	0.18354 (7)	0.0101 (8)
O6	O	1	0.3333	0.6667	0.32173 (13)	0.018 (2)
O7	O	1	0.6667	0.3333	0.21597 (11)	0.0088 (19)
O8	O	1	0.7482 (6)	0.8741 (3)	0.22475 (7)	0.0111 (14)
O9	O	1	0.7834 (3)	0.2166 (3)	0.25706 (6)	0.0114 (14)
O10	O	1	0	0	0.19203 (11)	0.003087
O11	O	0.53 (16)	0.3333	0.6667	0.1667	0.002 (2)
F1	F	0.47 (16)	0.3333	0.6667	0.1667	0.002 (2)
F2	F	1	0.6667	0.3333	0.3333	0.013 (2)
F3	F	0.993 (19)	0.3333	0.6667	0.12406 (10)	0.0082 (18)

(CO₃)²⁻. The intensity of this band is approximately half of the intensity of the band ν_1 (PO₄)³⁻. In stracherite the intensities of these two bands are roughly the same (Fig. 3).

Figure 3
Raman spectra of stracherite, ariegilatite and aravaite.

4.2. Structural investigations: average structure

For structural investigation, diffraction data of three crystals (A, B and C) of aravaite were collected. All crystals show distinct Bragg reflections which can be indexed using a trigonal unit cell (data for crystal A are listed in Table 2). Besides the Bragg reflections, one-dimensional diffuse intensities along **c*** are visible in the diffraction pattern. Fig. 4 shows the reconstructed (*h*0*l*) layer with one-dimensional diffuse intensities along **c*** (crystal A). Data of the same crystal were used for the crystal structure refinement. This particular crystal exhibits the least intense diffuse scattering and, therefore, was most suited for analysis of the average structure. The other crystals (B and C) exhibit differences in the diffuse intensities. However, Bragg reflections conforming to the given unit cell were also found in crystals B and C. Refined lattice parameters were not significantly different from crystal A.

The average structure of aravaite was solved using direct methods (SIR2004; Burla *et al.*, 2005). Subsequent least-squares refinements were performed using the program Jana2006 (Petříček *et al.*, 2014). Scattering coefficients were taken from *International Tables for Crystallography*, Volume C (Wilson,

Figure 4
Reciprocal space layer (*h*0*l*) of crystal A, as reconstructed from synchrotron diffraction data. The labelled group of reflections (2022–2034) exhibits a characteristic pattern of one-dimensional diffuse scattering and is used as an example for comparing experimental and simulated data.

Table 4

Anisotropic displacement parameters of aravaite.

Atom site	Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	Ba	0.0142 (3)	0.0142 (3)	0.0135 (4)	0.00711 (16)	0	0
Ca1	Ca	0.0017 (5)	0.0015 (6)	0.0164 (7)	0.0008 (3)	−0.0007 (2)	−0.0014 (4)
Ca2	Ca	0.0033 (6)	0.0028 (5)	0.0201 (8)	0.0016 (3)	−0.0010 (4)	−0.0005 (2)
Ca3	Ca	0.0023 (5)	0.0034 (6)	0.0119 (7)	0.0017 (3)	0.0006 (2)	0.0012 (4)
Na3	Na	0.0023 (5)	0.0034 (6)	0.0119 (7)	0.0017 (3)	0.0006 (2)	0.0012 (4)
T1	Si	0.0003 (5)	0.0003 (5)	0.0058 (9)	0.0002 (3)	0	0
T3	Si	0.0003 (5)	0.0003 (5)	0.0058 (9)	0.0002 (3)	0	0
T4	P	0.0069 (10)	0.0069 (10)	0.0051 (14)	0.0035 (5)	0	0
O1	O	0.022 (2)	0.022 (2)	0.010 (3)	0.013 (2)	−0.0006 (10)	0.0006 (10)
O2	O	0.014 (2)	0.014 (2)	0.008 (4)	0.0072 (12)	0	0
O3	O	0.0065 (15)	0.0035 (19)	0.047 (3)	0.0017 (10)	−0.0052 (10)	−0.010 (2)
O4	O	0.013 (2)	0.013 (2)	0.005 (4)	0.0066 (11)	0	0
O6	O	0.021 (3)	0.021 (3)	0.012 (4)	0.0104 (14)	0	0
O7	O	0.009 (2)	0.009 (2)	0.008 (4)	0.0046 (11)	0	0
O8	O	0.0023 (18)	0.0063 (14)	0.023 (3)	0.0011 (9)	0.0020 (16)	0.0010 (8)
O9	O	0.0129 (15)	0.0129 (15)	0.012 (2)	0.0092 (18)	−0.0013 (8)	0.0013 (8)
F2	F	0.016 (3)	0.016 (3)	0.007 (4)	0.0079 (14)	0	0
F3	F	0.008 (2)	0.008 (2)	0.009 (3)	0.0038 (10)	0	0

1995). Atom coordinates, isotropic displacement parameters and site occupancies for the average structure of the new mineral are presented in Table 3, anisotropic displacement parameters in Table 4, and selected bond distances in Table 5.

Bond-valence sum calculations are used to evaluate the valence of anion sites and, therefore, to identify fluorine and oxygen positions (Altermatt & Brown, 1985). The resulting structure model was refined using 85 parameters and 1291 independent reflections. Most of the atoms were described using anisotropic displacement parameters. Some atoms were modelled using isotropic displacement parameters, *e.g.* the sites with disorder such as T5, O11/F1. The notable high peak in the residual electron density is located 0.26 Å from the O10 atom (at the T3 tetrahedra) and does not represent a modellable atom position. The final R1 value of the refinement is 0.082, which is considerably larger than what we obtained in refinements of stracherite and ariegilatite (measured under comparable conditions, $R1 \simeq 0.02$). We attribute the larger R value, as well as the high residual electron density, to the stacking disorder, which obviously is present in the structure.

The structure of the mineral aravaite, $\text{Ba}_2\text{Ca}_{18}[(\text{SiO}_4)_6(\text{PO}_4)_3(\text{CO}_3)]\text{F}_3\text{O}$, can be described as a stacking of three different modules along [001]: T-layers $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$, triple antiperovskite (tAP) layers $\{(\text{F}_2\text{O}(\text{Ca}_{12})(\text{SiO}_4)_4)^{4+}$ and single antiperovskite (sAP) layers $\{(\text{FCa}_6)(\text{SiO}_4)_2\}^{3+}$ (Fig. 1). The modules are stacked in the sequence of T–sAP–T–tAP–.... This fragment of the sequence repeats three times within the unit cell. Along the c direction, the sum of all modules equals the sum of one unit cell of stracherite [three T-layers of $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$ and three sAP layers $\{(\text{FCa}_6)(\text{SiO}_4)_2\}^{3+}$] plus one unit cell of ariegilatite [three T-layers of $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$ and three tAP layers $\{(\text{F}_2\text{O}(\text{Ca}_{12})(\text{SiO}_4)_4)^{4+}$] (Fig. 1).

Comparing the structural model of aravaite to the structures of stracherite and ariegilatite, we can say that the refinement is essentially correct and represents a valid model

of the average structure, even though the R1 value seems not to be satisfying considering the refinement using synchrotron data.

The new mineral aravaite has six T-layers of $\{\text{Ba}(\text{PO}_4)_{1.5}(\text{CO}_3)_{0.5}\}^{3.5-}$, composed of BaO_6 octahedra, which are connected by two symmetry-independent PO_4 tetrahedra. One of the tetrahedra (T4) has an average P–O distance of 1.549 Å, the other (T5) shows smaller distances with an average of 1.472 Å. Therefore, it can be assumed that substitution by CO_3 groups takes place on T5. Occupational and positional disorder of PO_4/CO_3 at the T5 site results in unusual small bond distances with values somewhat intermediate between optimal P–O $\simeq 1.53$ Å and C–O $\simeq 1.28$ Å bond lengths (Shannon, 1976; Huminicki &

Hawthorne, 2002; Krivovichev, 2009). This substitution mechanism was found in stracherite and is discussed by Galuskin *et al.* (2018b).

The T-layers in stracherite and ariegilatite also contain two PO_4 tetrahedra; however, in these structures they are related by symmetry. In ariegilatite, the P–O distances average an unremarkable 1.547 Å, whereas in stracherite smaller values [3×1.4722 (2) and 1.5400 (4) Å] occur due to substitution of CO_3 (40% of PO_4 is replaced by CO_3). The planar $(\text{CO}_3)^{2-}$ groups are not observed in the base plane of substituted tetrahedra, as expected, but statistically distributed over three equivalent positions, parallel to three faces. This was confirmed by structural refinement and Raman spectroscopy investigations (Galuskin *et al.*, 2018b). The substitution of CO_3 groups for PO_4 tetrahedra in stracherite results in cation and anion disorder, characterized by splitting of Ca and O atom in adjacent layer. However, in aravaite we cannot model this local environment as detailed as in stracherite, because of the stacking fault disorder which limits the quality of the refinement. Nevertheless, analysis of the oxygen atoms surrounding T5, shows that the O1 site is depleted ($\sim 12\%$ vacancies), whereas O2 exhibits full occupancy. This is in agreement with the CO_3 substitution mechanism observed in stracherite. As no additional peaks of electron density were observed in the environment of T5, carbon was placed together with P on the T5 site. The small amount of sulfur (0.24 apfu) is assumed to be refined in sum with phosphorus due to the similar scattering power. Occupational parameters were refined to 54% for P and 46% for C, supporting the results of the chemical analysis (Table 1) and charge density calculation. The refined O1 vacancies account for 36% of CO_3 triangles only. The difference is probably caused by inaccuracy of the refinement of the involved occupancies.

The single antiperovskite (sAP) layers are built of F1Ca_6 octahedra and SiO_4 tetrahedra. They are equivalent to those found in stracherite and gazeevite. The same sAP layers can

Table 5
Distances and bond valences.

Bonds	Distance (Å)	Bond valence contribution
Ba1—O1 ×3	2.864 (4)	0.181
Ba1—O3 ×3	3.251 (5)	0.073
Ba1—O8 ×3	3.398 (5)	0.049
Ba1—O9 ×3	2.815 (3)	0.239
Average	3.082	
BVS		1.628
Ca1—O2	2.418 (4)	0.294
Ca1—O7	2.359 (4)	0.347
Ca1—O8 ×2	2.395 (5)	0.314
Ca1—O9 ×2	2.464 (3)	0.261
Ca1—F3	2.546 (4)	0.148
Average	2.434	
BVS		1.939
Ca2—O1 ×2	2.563 (4)	0.173
Ca2—O3 ×3	2.971 (6)	0.066
Ca2—O4	2.393 (4)	0.316
Ca2—O6	2.285 (3)	0.423
Ca2—F2	2.5507 (12)	0.147
Average	2.342	
BVS		1.996
Ca3—O5 ×3	2.515 (5)	0.227
Ca3—O8	2.616 (5)	0.173
Ca3—O10	2.2170 (16)	0.509
Ca3—O11	2.3317 (12)	0.196
Ca3—F1	2.3317 (12)	0.126
Ca3—F3	2.451 (4)	0.192
Average	2.390	
BVS		2.174
Na3—O5 ×3	2.515 (5)	0.146
Na3—O8	2.616 (5)	0.111
Na3—O10	2.2170 (16)	0.327
Na3—O11	2.3317 (12)	0.126
Na3—F1	2.3317 (12)	0.081
Na3—F3	2.451 (4)	0.123
Average	2.390	
BVS		1.395
T1—O5 ×3	1.621 (4)	1.008
T1—O7	1.636 (8)	0.968
Average	1.625	
BVS		3.992
T2—O3 ×3	1.607 (5)	1.047
T2—O6	1.606 (9)	1.049
Average	1.607	
BVS		4.191
T3—O8 ×3	1.610 (4)	1.038
T3—O10	1.747 (7)	0.718
Average	1.644	
BVS		3.831
T4—O4	1.545 (8)	1.214
T4—O9 ×3	1.551 (3)	1.197
Average	1.549	
BVS		4.803
T5p—O1 ×3	1.475 (4)	1.271
T5p—O2	1.463 (9)	1.504
Average	1.472	
BVS		5.316
T5c—O1 ×2	1.475 (4)	1.271
T5c—O2	1.463 (9)	1.504
Average	1.471	
BVS		4.046

be found in the other minerals of the zadovite group: zadovite and aradite. However in these minerals, SiO₄ tetrahedra are partly substituted by phosphate and vanadate tetrahedra, respectively.

The same kind of layers was described earlier for a number of minerals exhibiting elements of hexagonal antiperovskite structures (Sokolova *et al.*, 1999; Sokolova & Hawthorne, 2001; Krivovichev, 2007).

Employing bond-valence sum calculations, fluorine and oxygen are assigned to anion sites in the tAP layers (Table 5). Fluorine resides on the two outer octahedral sites (Fig. 1), whereas the anion site in the central octahedra is shared by fluorine and oxygen. In contrast to aravaite, ariegilite (and nabimusaite) exhibit an ordered anion distribution, with oxygen residing in the centre and fluorine on the two outer octahedral sites. For charge compensation, the Ca sites (Ca3, Table 3) coordinating the inner octahedral site are partly substituted by Na. Similar behaviour is already observed in two other compounds: in arctite, BaCa₇Na₅(PO₄)₆F₃ (Sokolova *et al.*, 1984; Sokolova & Hawthorne, 2001), all three positions are occupied by F and in the isostructural synthetic compound Ca_{5.45}Li_{3.55}[SiO₄]₃O_{0.45}F_{1.55} (Krüger, 2010), the central anion position is also shared by O and F.

5. Stacking faults and modelling of disorder

The crystal structure of aravaite can be described as an alternating sequence of ariegilite (T–tAP) and stracherite (T–sAP) blocks. Considering the presence of one-dimensional diffuse scattering, an obvious explanation is the stacking faults which disturb the ordered (alternating) sequence of ariegilite and stracherite blocks. This hypothesis is further supported by the fact that both structures (ariegilite and stracherite) are formed in similar conditions and are even observed intergrown (Fig. 2b).

In order to test the aforementioned hypothesis of disorder within the sequence of T–tAP and T–sAP blocks, structural models of these two blocks were prepared starting from the respective structures. The *c* lattice parameter of the stracherite block (T–sAP) is 8.35 Å ($\approx c_{\text{sta}}/3$), and for the ariegilite block it is 13.74 Å ($\approx c_{\text{ari}}/3$). The model of the stracherite block contains 28 atoms, whereas the model of the ariegilite block includes 46 atoms. The earlier mentioned disorder (CO₃ substitution) was neglected. By stacking T–tAP or T–sAP blocks only, the structures of ariegilite or stracherite are obtained, respectively. Stacking these blocks alternately results in the structure of aravaite. Stacking has to be done by using a vector of ($\frac{2}{3}, \frac{1}{3}, c_{\text{block}}$) to emulate the *R*-centring of the structures and to keep the structure of the interface unchanged. The software *DISCUS* (version 5.14; Proffen & Neder, 1999; Neder & Proffen, 2008) was utilized to create stacking sequences with different degrees of disorder. A Markov chain growth disorder model was employed, which is defined by a right stochastic matrix containing the transition probabilities between adjacent blocks (*e.g.* $P_{\text{sta-ari}}$ is the

probability for an ariegilatite block following a stracherite block):

$$M = \begin{pmatrix} P_{\text{sta-sta}} & P_{\text{sta-ari}} \\ P_{\text{ari-sta}} & P_{\text{ari-ari}} \end{pmatrix} = \begin{pmatrix} 1 - \alpha & \alpha \\ 1 - \alpha - \beta & \alpha + \beta \end{pmatrix}.$$

The growth parameters α and β are related to the elements of the stochastic matrix as shown above (for details, see *e.g.*, Welberry, 2004; Neder & Proffen, 2008).

In this case both blocks have to be present in the same amount (constrained by chemical composition). Consequently, $\beta = 1 - 2\alpha$, because of the known relation between α , β and the concentration of block types. The growth parameter α represents the probability of a change in the block type, whereas β denotes the correlation between neighbouring blocks.

A series of models for different growth parameters was created. Each model was simulated 750 times using 25 000 blocks. X-ray scattering was calculated using a Fourier transform of each simulation as described by Neder & Proffen (2008) and subsequently the line profiles of all 750 simulations were summed up. The 20/ intensity profiles for models with negative to zero correlation are shown in Fig. 5. Simulations with positive correlation (ordering towards domains of stracherite and ariegilatite) are shown in Fig. 6. For a qualitative comparison of the diffuse scattering a part of the 20/ line was chosen. Between $l = -37$ and $l = -17$ some characteristic diffuse intensities can be observed in the experimental data of crystal A (Figs. 4 and 7). The highest intensities are located between the -34 and -31 Bragg reflections. However, between all neighbouring pairs of Bragg reflections diffuse scattering can be observed. A minimum is located at the right side of -28 , towards -25 the intensity is slightly increasing. The minor peak at *circa* $l = -20$ is most likely an 'alien' reflection, belonging to another crystal grain. The simulations (shown in Fig. 5) explain all significant features of the diffuse

scattering observed in Fig. 7. However, none of the simulated growth parameters result in a perfect match. For example, none of the simulations reproduce the observed intensity relations between -34 , -28 and -25 . A certain range of α seems to be required to obtain a better fit. Measurements on several crystals have shown that the degree of order is quite variable; therefore, also within a single crystal variations are likely to occur.

The intensity distribution along 20/ in crystals B and C is different. Fig. 8 shows that crystal B exhibits the same features as crystal A (Fig. 7); however, the intensities on -28 and -25 are reduced, whereas -31 seems stronger compared with -34 . This is what can be expected from increased disorder (compare with Fig. 5). Crystal C shows additional peaks (Fig. 8), which at a first glance suggest a superstructure. A more detailed investigation shows that the strongest of them may be explained by the existence of ordered domains of ariegilatite. The simulations for large positive correlation (shown in Fig. 6) produce intensities on positions corresponding to the lattices of stracherite and ariegilatite, because increasing correlations result in larger domains of stracherite and ariegilatite. Fig. 9 shows the diffuse scattering on 20/ for $\alpha = 0.9, 0.5$ and 0.1 . Simulations of the ordered structures of ariegilatite, stracherite and aravaite were used to assign peaks of the disordered simulation ($\alpha = 0.9$ and 0.1) to the respective structures. Reciprocal lattice units (r.l.u.) refer to c of aravaite. With the guidance of Fig. 9, the additional reflections of crystal C (Fig. 8) may be explained. The intensity at $l = -32.1$ occurs at the same position where a peak of ariegilatite domains would be expected. The same is true for the small peak at -17.7 . However, the intense stracherite peak expected at -21.1 is not visible in the data of crystal C. Also, the stracherite peak at -29 (Fig. 9) does not fit to the position of a weak intensity in Fig. 8 (at $l = -29.5$). Two more small

Figure 5
Intensity distribution along the reciprocal space line 20/ obtained from simulations with $\alpha = 0.9, \dots, 0.5$ (r.l.u. is reciprocal lattice units). This series shows the effect of increasing disorder.

Figure 6
Intensity distribution along the reciprocal space line 20/ obtained from simulations with positive correlations ($\beta = 0.0, \dots, 0.8$) (r.l.u. is reciprocal lattice units). This series shows the effect of increasing order towards larger domains of stracherite and ariegilatite.

intensities at -23.7 and -22.4 cannot be explained. One possible reason for these observations is that besides ariegilite domains, domains of a stracherite-enriched superstructure exist. Another explanation for the missing intensity of the stracherite peaks may be a deviation in the chemical composition of the specific grain. However, without further simulations and experimental work, such as transmission electron microscopy, this is speculation. The fact is that crystal C additionally shows all features of a fairly disordered crystal (such as crystal B). Therefore, it has to contain a large variation in its disorder.

Figure 7
Intensity distribution along reciprocal space line $20l$ of crystal A (r.l.u. is reciprocal lattice units). Two symmetry-equivalent lines are shown.

Figure 8
Intensity distribution along reciprocal space line $20l$ of crystal B and C (r.l.u. is reciprocal lattice units). For crystal B two symmetry-equivalent lines are drawn. Crystal C exhibits extra reflections, the strongest of which can be explained by ariegilite (ARI) domains. Positions at which stracherite (STA) peaks could be expected are indicated. Compare with the simulations shown in Fig. 9.

Figure 9
The intensity distribution along $20l$ for three different simulations ($\alpha = 0.9, 0.5$ and 0.1) (r.l.u. is reciprocal lattice units). The first simulation is close to an ordered structure of aravaite. The second exhibits a random sequence ($\beta = 0$), and the third a strong positive correlation, which results in domains of stracherite (STA) and ariegilite (ARI). Peaks are labelled with the phase of major intensity contribution.

Nonetheless, the simulations prove that the diffuse scattering in aravaite is caused by a faulty sequence of ariegilite and stracherite modules. Furthermore, the simulations show that disorder has a major impact on the intensities of Bragg reflections. This can be seen in the rather high- R values and high residual electron density of the structure refinement.

6. Conclusion

Aravaite brings another structure type into the list of known intercalated antiperovskites. Therefore, a new group is needed for their classification, as it fits neither into the nabimusaite group nor into the zadovite group. A *mixed structures* group within the arctite supergroup was proposed by Galuskin *et al.* (2018a). Similar mixed structures may exist between other members of the nabimusaite and zadovite group.

The observed disorder by stacking faults is an interesting case with two layers of different thickness. The presented disorder model can be applied to similar cases, which may exist within the arctite supergroup. It could also be adapted to cases with an unequal ratio of the different modules.

One interesting question is to what extent of the disorder a meaningful average structure model can be refined from Bragg diffraction data. In this case, the structure refinement of the most ordered crystal (least-diffuse intensities) still results in a complete structure model. However, limits of the model become visible. The details of the CO_3 substitution could not be revealed as detailed as in ordered stracherite. Furthermore, some anisotropic displacement parameters became extreme or even physically meaningless. A test refinement with crystal B resulted in an increased $R1$ of more than 0.12 with deteriorated quality of the structure model. However, the basic structure can still be derived.

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