

CHIYOKOITE, $\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$, A NEW ETTRINGITE-GROUP MINERAL FROM THE FUKA MINE, OKAYAMA PREFECTURE, JAPAN

INNA LYKOVA[§]

*Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada
Faculty of Geology, Moscow State University, Vorobyovy Gory, 119992 Moscow, Russia*

NIKITA V. CHUKANOV

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Oblast 142432, Russia

IGOR V. PEKOV AND VASILII O. YAPASKURT

Faculty of Geology, Moscow State University, Vorobyovy Gory, Moscow 119992, Russia

LEONID A. PAUTOV

*Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskiy Prospekt 18-2, Moscow 117901, Russia
Institute of Mineralogy, Urals Branch of Russian Academy of Sciences, Miass, Chelyabinsk Oblast 456300, Russia*

VLADIMIR YU. KARPENKO AND DMITRY I. BELAKOVSKIY

Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskiy Prospekt 18-2, Moscow 117901, Russia

DMITRY A. VARLAMOV

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Oblast 142432, Russia

SERGEY N. BRITVIN

Department of Crystallography, St. Petersburg State University, University Embankment 7/9, St. Petersburg 199034, Russia

KATHARINA S. SCHEIDL

Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, Vienna A-1090, Austria

ABSTRACT

The new ettringite-group mineral chiyokoite, ideally $\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$, was found in a hydrothermally altered calc-silicate skarn at the Fuka mine, Okayama Prefecture, Japan. Associated minerals are calcite, henmilite, and tacharanite. Chiyokoite occurs as hexagonal prismatic crystals up to 30 μm long and up to 20 μm thick. The major forms are the hexagonal prism $\{10\bar{1}0\}$ and monohedra $\{0001\}$ and $\{00\bar{1}\}$. The crystals are combined in clusters which form friable nests up to 1 cm across. The mineral is pink to colorless with white streak and vitreous luster. The cleavage is parallel to $\{10\bar{1}0\}$ and $\{0001\}$, good. The fracture is stepped. D_{meas} is 1.85(1) g/cm^3 , D_{calc} is 1.85 g/cm^3 . Chiyokoite is optically uniaxial (–), $\omega = 1.523(2)$ and $\epsilon = 1.492(3)$ (589 nm). The infrared spectrum is reported. The chemical composition (wt.%) is CaO 27.56, B_2O_3 3.47, Al_2O_3 3.05, Fe_2O_3 0.12, As_2O_3 4.77, MnO_2 0.32, SiO_2 6.55, SO_3 0.76, H_2O 46.3, CO_2 7.30, total 100.2. The empirical formula calculated on the basis of 3 Ca *apfu* is $\text{H}_{31.37}\text{Ca}_3(\text{Si}_{0.67}\text{Al}_{0.37}\text{Mn}^{4+}_{0.02}\text{Fe}^{3+}_{0.01})_{\Sigma 1.07}(\text{C}_{1.01}\text{B}_{0.61}\text{As}^{3+}_{0.29}\text{S}_{0.06})_{\Sigma 1.97}\text{O}_{24.19}$. The simplified general formula is $\text{Ca}_3(\text{Si,Al})(\text{CO}_3,\text{AsO}_3)[\text{B}(\text{OH})_4,\text{AsO}_3](\text{OH})_6 \cdot 12\text{H}_2\text{O}$. Chiyokoite is hexagonal, $P6_3$, $a = 11.0119(5)$, $c = 10.5252(6)$ Å, and $V = 1105.3(1)$ Å³. The strongest reflections of the powder X-ray diffraction pattern [$d, \Delta(hkl)$] are: 9.53(100)(100), 5.50(24)(110), 4.618(11)(102), 3.812(23)(112), 3.412(15)(211), 2.726(14)(302),

[§] Corresponding author e-mail address: ilykova@nature.ca

2.521(19)(123), and 2.172(13)(320,402,223). The crystal structure, refined from single-crystal X-ray diffraction data [$R1(F) = 0.042$], is based on $[\text{Ca}_3(\text{Si},\text{Al})(\text{OH})_6(\text{H}_2\text{O})_{12}]$ columns parallel to the c axis with $\text{B}(\text{OH})_4^-$ and CO_3^{2-} and admixed AsO_3^{3-} anionic groups in channels between the columns. The mineral is named in honor of Professor Chiyoko Henmi (1949–2018).

Keywords: chiyokoite, ettringite group, new mineral, crystal structure, Fuka mine, Japan.

INTRODUCTION

Members of the ettringite group are trigonal and hexagonal minerals with the general formula $\text{Ca}_6[\text{M}_2(\text{OH},\text{O})_{12}]\text{A}_{2-3}\cdot n\text{H}_2\text{O}$, where $M = \text{Si}, \text{Al}, \text{Cr}^{3+}, \text{Ge}^{4+}, \text{Fe}^{3+}, \text{or } \text{Mn}^{4+}$; $A = \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{SO}_3^{2-}, \text{HPO}_4^{2-}, \text{CrO}_4^{2-}, \text{or } \text{B}(\text{OH})_4^-$; and $n = 22\text{--}26$. There are three structure types. The first is characterized by disordered A anions and $P6_3/m$ space group. In the second structure type the A anions are ordered, lowering the symmetry to $P6_3$. The $\text{Ca}:A$ ratio is 3:2 in both types. The third structure type includes trigonal ettringite-group minerals (space group $P31c$) characterized by a doubled c parameter and a $\text{Ca}:A$ ratio of 2:1 (Chukanov *et al.* 2016, Juroszek *et al.* 2020). Six minerals belong to the second structure type: jouravskite, $\text{Ca}_3\text{Mn}^{4+}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Granger & Protas 1969, Chukanov *et al.* 2019); thaumasite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Effenberger *et al.* 1983, Martucci & Cruciani 2006); hielscherite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{SO}_3)(\text{OH})_6\cdot 11\text{H}_2\text{O}$ (Pekov *et al.* 2012); imayoshiite, $\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Nishio-Hamane *et al.* 2015); tatarinovite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Chukanov *et al.* 2016); and the new species described in this paper, chiyokoite, $\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5\cdot 12\text{H}_2\text{O}$.

Chiyokoite is named in honor of Professor Chiyoko Henmi (1949–2018), who worked in the Department of Earth Science at Okayama University. Professor Henmi made significant contributions to the mineralogy of skarn minerals from the Fuka mine, including the discovery of several new minerals: bicchulite (Henmi *et al.* 1973), clinotobermorite (Henmi & Kusachi 1992), fukalite (Henmi *et al.* 1977), kusachiite (Henmi 1995), morimotoite (Henmi *et al.* 1995), oyelite (Kusachi *et al.* 1980), parasibirskite (Kusachi *et al.* 1998), and takedaite (Kusachi *et al.* 1995). Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2019–054).

The data for the new mineral description were obtained from several specimens which are considered cotypes. Cotype I was deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5412/1; the catalogue number in the systematic collection is 96818. Cotype II was

deposited in the collection of the Canadian Museum of Nature, Ottawa, Canada, where the catalogue number is CMNMC 87294.

OCCURRENCE AND GENERAL APPEARANCE

Chiyokoite was found in specimens collected by one of the authors (IVP) in July 2006 at the Fuka mine, Fuka, Bicchu-cho, Takahashi City, Okayama Prefecture, Japan. It is a low-temperature hydrothermal mineral formed in cavities of a hydrothermally altered, boron-bearing, low-Fe calc-silicate skarn (Kusachi *et al.* 1999) together with calcite, henmilite, and tacharanite.

Chiyokoite occurs as hexagonal prismatic crystals up to 30 μm long and up to 20 μm thick (Fig. 1a). The major forms of the hexagonal pyramidal crystals are the hexagonal prism $\{10\bar{1}0\}$ and monohedra $\{0001\}$ and $\{000\bar{1}\}$; narrow faces of the hexagonal pyramid $\{h0il\}$ are observed on some crystals. The crystals are combined in clusters (Fig. 1b) which form, together with intimately associated calcite, friable nests (Fig. 2) up to 1 cm across and up to 1 mm thick in tacharanite-calcite incrustations (Fig. 3).

PHYSICAL PROPERTIES AND OPTICAL DATA

Chiyokoite is pink to colorless. The streak is white. The luster is vitreous. The mineral is non-fluorescent under ultraviolet light. The Mohs hardness was not determined, as the crystals are very small. The cleavage is parallel to $\{10\bar{1}0\}$ and $\{0001\}$, good. The fracture is stepped. Density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 1.85(1) g/cm^3 . It was measured in a small shallow hole in a petrographic slide under a microscope. Density calculated using the unit-cell volume refined from the single-crystal XRD data is 1.84 g/cm^3 using the empirical formula and 1.85 g/cm^3 using the structural formula (we were unable to reliably locate H sites in the structure of chiyokoite; therefore, H atoms were added manually to calculate the density).

In transmitted light, chiyokoite is colorless and non-pleochroic. It is optically uniaxial (–), $\omega = 1.523(2)$, and $\epsilon = 1.492(3)$ (589 nm). Under a microscope most chiyokoite grains are of rectangular shape demonstrating two directions of cleavage: one parallel to the optical axis and another one perpendic-

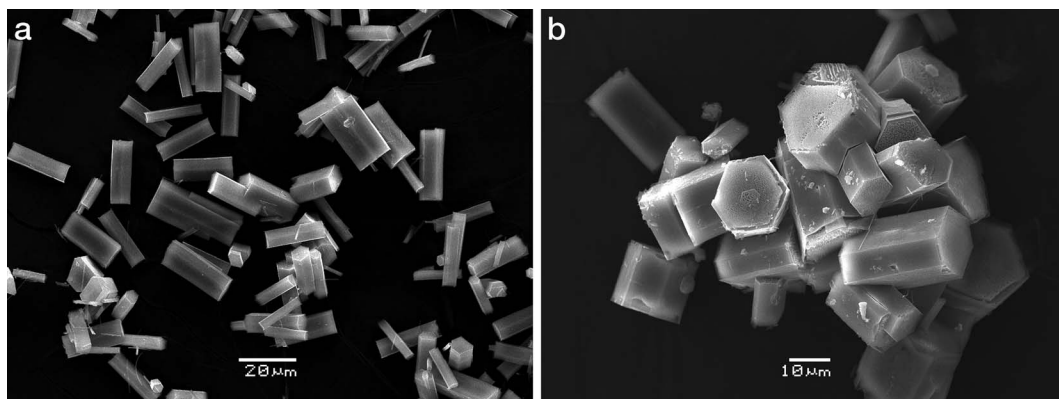


FIG. 1. Crystals of (a) chiyokoite and (b) their cluster. SEM (SE) images.

ular to it. Rectangular grains have straight extinction, and most of them have negative elongation. Some grains are of hexagonal shape; these are isotropic and show an interference figure perpendicular to the optical axis.

INFRARED SPECTROSCOPY

In order to obtain the infrared (IR) absorption spectra of chiyokoite and related minerals (Fig. 4), powdered samples were mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1} . A total of 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The band assignment is given in Figure 4. The IR spectrum of chiyokoite contains strong bands of H_2O

molecules and OH^- , CO_3^{2-} , and AsO_3^{3-} groups, as well as characteristic bands of $\text{B}(\text{OH})_4^-$ groups and $\text{Si}(\text{OH})_6^{2-}$ octahedra, and relatively weak bands for SO_4^{2-} groups and $\text{Al}(\text{OH})_6^{3-}$ octahedra. The strong band at 674 cm^{-1} corresponds to $\text{As}^{3+}\text{-O}$ stretching vibrations, in accordance with the trivalent state of As as determined by the crystal structure refinement. The band assignment was made in accordance with Chukanov & Chervonnyi (2016).

In the IR spectra of S-dominant ettringite-group minerals, strong IR bands in the ranges 1085–1115 and $590\text{--}680\text{ cm}^{-1}$ (Fig. 4) correspond to asymmetric stretching and bending vibrations of SO_4^{2-} anions, respectively (Pushcharovsky *et al.* 2004, Pekov *et al.* 2012, Chukanov *et al.* 2012, 2016, 2019). In the IR spectrum of chiyokoite, the intensity of the band of S–O stretching vibrations (at 1087 cm^{-1}) is relatively low, in accordance with a low sulfur content in this

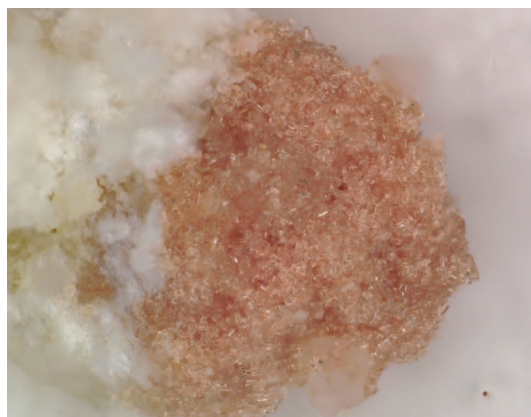


FIG. 2. Cluster of pink prismatic crystals of chiyokoite on calcite. FOV 1.1 mm. CMNC 87294. Photo: Paul Sokoloff and Inna Lykova.



FIG. 3. Fine-grained pink chiyokoite aggregates with colorless to greyish calcite and snow-white tacharanite. FOV 15 mm. Photo: Igor Pekov and Anatoly Kasatkin.

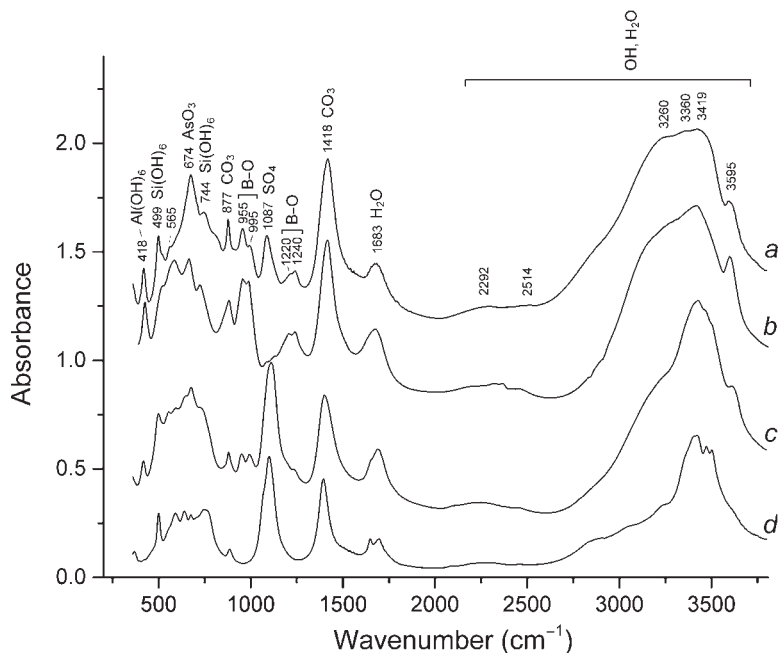


FIG. 4. Infrared spectra of (a) chiyokoite, $\text{Ca}_3(\text{Si,Al})(\text{CO}_3,\text{AsO}_3)[\text{B}(\text{OH})_4,\text{AsO}_3](\text{OH})_6 \cdot 12\text{H}_2\text{O}$; (b) imayoshiite, $\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$ (drawn using data from Nishio-Hamane *et al.* 2015); (c) tatarinovite, $\text{Ca}_3\text{Al}(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$ (the holotype sample: Chukanov *et al.* 2016); and (d) thaumasite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$, from an outcrop at the mouth of the Uraveli river, near Akhaltsikhe, Georgia. The spectra have been offset for comparison.

mineral. Consequently, the strong band at 674 cm^{-1} cannot be assigned to SO_4^{2-} anions.

The arsenate anion AsO_4^{3-} is characterized by a strong and broad band of As^{5+}O stretching vibrations in the range $780\text{--}920\text{ cm}^{-1}$ which can be split into several components, while strong IR bands corresponding to As^{3+}O stretching vibrations of the isolated arsenite anion AsO_3^{3-} are observed in the range $500\text{--}700\text{ cm}^{-1}$ (see, *e.g.*, Chukanov 2014, Chukanov & Chervonnyi 2016, Chukanov & Vigasina 2020). In the range $780\text{--}920\text{ cm}^{-1}$, the IR spectrum of chiyokoite contains only a weak shoulder at 800 cm^{-1} and a narrow single band with a medium intensity at 877 cm^{-1} which is a characteristic feature of carbonate-bearing ettringite-group minerals and corresponds to nondegenerate out-of-plane bending vibrations of CO_3^{2-} . Thus, the presence of a significant amount of AsO_4^{3-} anions in chiyokoite should be excluded, and the strong band at 674 cm^{-1} is assigned to stretching vibrations of AsO_3^{3-} anions.

CHEMICAL DATA

Chemical data for chiyokoite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-

dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University) with an acceleration voltage of 20 kV, a beam current of 6.5 nA, and a beam diameter of $5\text{ }\mu\text{m}$. The following standards were used: lorenzenite (Si), wollastonite (Ca), Mn (Mn), Fe (Fe), Hlb-143965 (Al), LaB₆ (B), InAs (As), and FeS₂ (S).

The B content was also determined using inductively coupled plasma - optical emission spectrometry (ICP-OES) from a 5.07 mg sample. The sample was preliminarily decomposed by fusion with a mixture of analytical grade KNO_3 (5 mg) and Na_2CO_3 (100 mg) and subsequently dissolved and analyzed with an internal standard (In). This method of quantitative boron determination seems better than electron microprobe analysis for a mineral with a relatively low B content.

The H_2O and CO_2 contents were determined using a modification of the Pregl-Dumas method with chromatographical completion, performed with a Carlo Erba 1106 CHN-analyzer (equipped with a thermal conductivity detector and column, filled with Porapak QS; high-pure He used as a carrier; flash temperature $\sim 1800\text{ }^\circ\text{C}$) using a 0.593 mg sample. Benzoic acid, acetanilide, and sulphanilamide were

TABLE 1. CHEMICAL COMPOSITION OF CHIYOKOITE

Constituent	wt. %	Range	Stand. Dev.
CaO ¹	27.56	26.79–28.33	0.58
B ₂ O ₃ ^{1,2}	3.47 ²	3.12–4.27 ¹	
Al ₂ O ₃ ¹	3.05	2.34–3.91	0.56
Fe ₂ O ₃ ^{1,3}	0.12	0.07–0.17	0.04
As ₂ O ₃ ^{1,4}	4.77	3.97–5.60	0.53
MnO ₂ ^{1,3}	0.32	0.09–0.62	0.20
SiO ₂ ¹	6.55	5.62–7.51	0.67
SO ₃ ¹	0.76	0.46–1.02	0.21
H ₂ O	46.3		
CO ₂	7.30		
Total	100.2		

¹ From electron microprobe data (average of seven analyses).

² From ICP-OES data.

³ Minor admixtures of Mn and Fe are formally considered to be tetravalent and trivalent, respectively, by analogy with jouravskite, [Ca₃Mn⁴⁺(SO₄)(CO₃)(OH)₆·12H₂O] (Chukanov *et al.* 2019), and other ettringite-group minerals which contain Mn and Fe in high oxidation states only.

⁴ The trivalent state of arsenic was unambiguously determined from the structural data and IR spectrum.

used as standards. The obtained values are 7.30(4) wt.% CO₂ and 46.3(4) wt.% H₂O.

Analytical data are given in Table 1. Many ettringite-group minerals, including chiyokoite, easily dehydrate in vacuum, losing water in a matter of minutes, and are unstable under an electron beam (Chukanov *et al.* 2016); as a result, the measured totals of our WDS analyses were overstated relative to the actual values. Therefore, the data given in Table 1 were normalized based on the B content obtained via ICP-OES analysis.

The empirical formula calculated on the basis of 3 Ca atoms per formula unit (*apfu*) is H_{31.37}Ca₃(Si_{0.67}Al_{0.37}Mn⁴⁺_{0.02}Fe³⁺_{0.01})Σ_{1.07}(C_{1.01}B_{0.61}As³⁺_{0.29}S_{0.06})Σ_{1.97}O_{24.19}.

Chiyokoite readily dissolves in dilute HCl with effervescence at room temperature.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Powder X-ray diffraction data for chiyokoite were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector and using Debye-Scherrer geometry (*d* = 127.4 mm; CoK α -radiation). Unit-cell

parameters refined from the powder data are *a* = 11.0282(15), *c* = 10.5774(37) Å, and *V* = 1114.1(7) Å³. The indexed powder X-ray diffraction data are available as a supplementary file, Table S1¹.

Single-crystal X-ray studies were carried out using a STOE StadiVari diffractometer equipped with a Dectris PILATUS 300K pixel detector (MoK α radiation) at the Institute of Mineralogy and Crystallography, University of Vienna, Austria. The structure was refined to *R* = 0.042 on the basis of 1093 independent reflections with *I* > 2σ(*I*) using the SHELXL-2018/3 program package (Sheldrick 2015). The atomic coordinates of thaumasite, Ca₃Si(SO₄)(CO₃)(OH)₆·12H₂O (Jacobsen *et al.* 2003), were used as a starting model for the refinement. Crystal data, data collection information, and structure refinement details are given in Table 2; atom coordinates, equivalent displacement parameters, and site occupancy factors in Table 3; and selected interatomic distances in Table 4. A crystallographic information file (CIF) for chiyokoite is available as a supplementary file. The studied crystal demonstrated twinning by merohedry Class I (Nespolo & Ferraris 2000), with a twin domains ratio of 58:42.

DESCRIPTION OF THE CRYSTAL STRUCTURE

Chiyokoite is a structural analogue of thaumasite, Ca₃Si(SO₄)(CO₃)(OH)₆·12H₂O (Edge & Taylor 1971, Zemmann & Zobetz 1981, Effenberger *et al.* 1983, Jacobsen *et al.* 2003, Martucci & Cruciani 2006). Its crystal structure is based on [Ca₃(Si,Al)(OH)₆(H₂O)₁₂] columns parallel to the *c* axis (Fig. 5). The columns are formed by alternating (Si,Al)(OH)₆ octahedra and trimers of edge-sharing Ca(OH)₄(H₂O)₄ polyhedra. They are interconnected *via* hydrogen bonding with additional anion groups located in channels between the columns (Fig. 6). No doubled unit cell (*c* ~ 20 Å) and no lowering of the symmetry (*P*6₃ → *P*31*c*) were observed.

The C site has three-fold coordination. Based on the *c*_{ref} value [9.1] and chemical data, the occupation of the C site was constrained to 0.90 for C and 0.10 for As³⁺. Carbon and arsenic atoms occur in trigonal planar CO₃²⁻ groups and triangular pyramidal arsenite groups AsO₃³⁻, respectively. The occupation of the B site (the site occupied by S atoms in thaumasite) was fixed as 0.64 for B, 0.18 for As³⁺, and 0.18 for C. Boron atoms, the predominant component at the B site, occur in a B(OH)₄ tetrahedra. There are two possible

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document “Chiyokoite, CM58, 20-00030”.

TABLE 2. CRYSTAL DATA, DATA COLLECTION INFORMATION, AND STRUCTURE REFINEMENT DETAILS FOR CHIYOKOITE

Formula derived from the structure refinement	$\text{Ca}_3(\text{Si}_{0.64}\text{Al}_{0.36})[(\text{CO}_3)_{0.90}(\text{AsO}_3)_{0.10}]$ $[(\text{B}(\text{OH})_4)_{0.64}(\text{AsO}_3)_{0.18}(\text{CO}_3)_{0.18}](\text{OH})_6 \cdot 12\text{H}_2\text{O}$
Crystal system, space group, Z	Hexagonal, $P6_3$, 2
a (Å)	11.0119(5)
c (Å)	10.5252(6)
V (Å ³)	1105.3(1)
λ (MoK α) (Å), T (K)	0.71073, 293
Diffractometer	STOE StadiVari
θ range (°)	2.14–31.75
Crystal size (mm)	$0.005 \times 0.005 \times 0.02$
Absorption coefficient m (mm ⁻¹)	1.32
F_{000}	644
h, k, l range	$-14 \leq h \leq 14, -14 \leq k \leq 12, -13 \leq l \leq 14$
Reflections collected	11111
Unique reflections, R_{int}	1747, 0.0878
Unique reflections [$I > 2\sigma(I)$]	1093
Number of refined parameters	110
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0386P)^2]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
$R1$	0.042
$wR2_{\text{all}}(F^2)$	0.095
GoF	0.959
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e/Å ³)	0.62 / -0.41

orientations of the $\text{B}(\text{OH})_4$ tetrahedra, and their distribution is disordered, with 50% occupancy of the OB(1a) and OB(2a) sites, which represent the average positions for the O_B (32%), O_As (9%), and O_C

(9%) atoms, and with 32% occupancy of the OB(1b) and OB(2b) sites (Fig. 6, Table 3). The disorder of the triangular planar CO_3^{2-} groups and triangular pyramidal AsO_3^{3-} groups was ignored in the refinement

TABLE 3. COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS (U_{eq} , IN Å²) OF ATOMS AND SITE OCCUPANCIES FOR CHIYOKOITE

Site	Wyck	x	y	z	U_{eq}	s.o.f./site composition ¹
Ca	6c	0.19968(10)	0.00008(10)	0.2521(6)	0.0140(2)	1
Si	2a	0	0	0.0002(12)	0.0087(4)	$\text{Si}_{0.64}\text{Al}_{0.36}$
B	2b	1/3	2/3	0.0035(10)	0.0118(15)	$\text{B}_{0.64}\text{As}_{0.18}\text{C}_{0.18}$
C(As)	2b	1/3	2/3	0.5049(19)	0.023(3)	$\text{C}_{0.90}\text{As}_{0.10}$
O(1) = H ₂ O	6c	0.4067(5)	0.2556(5)	0.2455(14)	0.0306(12)	1
O(2) = H ₂ O	6c	0.2558(5)	0.4070(4)	0.2567(14)	0.0321(13)	1
O(3) = H ₂ O	6c	0.0027(11)	0.3435(11)	0.0806(11)	0.035(3)	1
O(4) = H ₂ O	6c	0.9974(9)	0.3389(10)	0.4311(9)	0.024(2)	1
O(5) = OH	6c	0.1311(10)	0.1295(10)	0.1082(7)	0.014(2)	1
O(6) = OH	6c	0.9980(7)	0.1314(12)	0.8969(7)	0.016(2)	1
OB(1a) = (OH,O)	6c	0.8130(11)	0.4309(13)	0.4561(16)	0.027(3)	0.50
OB(1b) = OH	2b	2/3	1/3	0.646(2)	0.006(4) ²	0.32
OB(2a) = (OH,O)	6c	0.8067(15)	0.3797(17)	0.547(2)	0.035(4)	0.50
OB(2b) = OH	2b	2/3	1/3	0.358(2)	0.007(4)	0.32
OC	6c	0.4679(6)	0.7338(7)	0.5026(12)	0.0397(15)	0.90
OAs	6c	0.439(5)	0.839(3)	0.451(5)	0.004(11) ²	0.10

¹ Based on the e_{ref} values and chemical data, taking also into account coordination polyhedra character and interatomic distances.

² U_{iso} .

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF CHIYOKOITE

Ca	—O(3)	2.393(12)
	—O(4)	2.438(11)
	—O(5)	2.444(8)
	—O(6)	2.450(8)
	—O(5)	2.469(9)
	—O(6)	2.479(9)
	—O(1)	2.589(5)
	—O(2)	2.593(5)
<Ca—O>		2.482
Si	—O(6)	1.819(13) × 3
	—O(5)	1.831(13) × 3
B	—OB(2a)	1.437(16) × 3
	—OB(1b)	1.50(2)
	—OB(1a)	1.506(13) × 3
	—OB(2b)	1.53(2)
C(As)	—OC	1.283(6) × 3
C(As)	—OAs	1.751(14) × 3

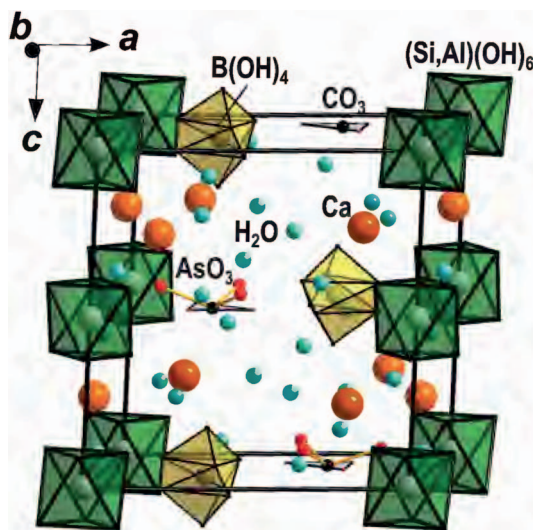


FIG. 6. General view of the crystal structure of chiyokoite. The unit cell is outlined.

owing to the low quality of the SXRD data ($R_{\text{int}} = 0.0878$).

The obtained structural formula of chiyokoite is $\text{Ca}_3(\text{Si}_{0.64}\text{Al}_{0.36})\{[(\text{B}(\text{OH})_4)_{0.64}(\text{AsO}_3)_{0.18}(\text{CO}_3)_{0.18}][(\text{CO}_3)_{0.90}(\text{AsO}_3)_{0.10}](\text{OH})_6 \cdot 12\text{H}_2\text{O}$ or, in the simplified form: $\text{Ca}_3(\text{Si},\text{Al})(\text{CO}_3,\text{AsO}_3)[\text{B}(\text{OH})_4,\text{AsO}_3](\text{OH})_6 \cdot 12\text{H}_2\text{O}$.

ENDMEMBER FORMULA

Chiyokoite, $\text{Ca}_3(\text{Si},\text{Al})(\text{CO}_3,\text{AsO}_3)[\text{B}(\text{OH})_4,\text{AsO}_3](\text{OH})_6 \cdot 12\text{H}_2\text{O}$, is a $\text{B}(\text{OH})_4$ -dominant analogue

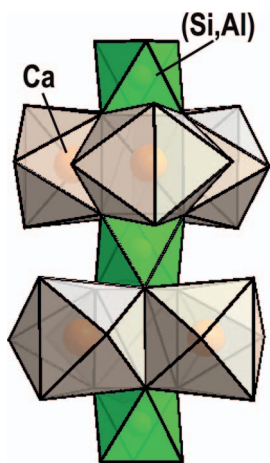


FIG. 5. Column composed of (Si,Al)-centered octahedra and trimers of Ca-centered polyhedra in the crystal structure of chiyokoite.

[with $\text{B}(\text{OH})_4 > \text{SO}_4$] of thaumasite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$ (Anthony *et al.* 1995, Jacobsen *et al.* 2003, Martucci & Cruciani 2006); a Si-dominant analogue (with $\text{Si} > \text{Al}$) of imayoshiite, $\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$ (Nishio-Hamane *et al.* 2015); and a CO_3 -dominant analogue (with $\text{CO}_3 > \text{SO}_4$) of buryatite, $\text{Ca}_3(\text{Si},\text{Fe}^{3+})(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH},\text{O})_6 \cdot 12\text{H}_2\text{O}$ (Malinko *et al.* 2001; Table 5). There are several substitution schemes that could result in an ettringite-group mineral with dominant Si, B, and C, including the substitutions (1) Si for Al; (2) B for As^{3+} , C, or S^{6+} ; and (3) $(\text{OH})^-$ for O^{2-} . Therefore, different idealized endmember formulae, e.g., $\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}_3\text{Si}(\text{CO}_3)\{[\text{B}(\text{OH})_4]_{0.5}(\text{AsO}_3)_{0.5}\}(\text{OH})_6 \cdot 12\text{H}_2\text{O}$, could be written for chiyokoite. While the former formula includes a substitution $[(\text{OH})^- \text{ for } \text{O}^{2-}]$ that has not been observed in the mineral studied in this work, it better represents the distribution of the main cations than the latter one. As^{3+} is not a dominant cation at any site, and so it should not be considered a dominant component in chiyokoite. For this reason, we consider $\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$ the definitive end-member formula of chiyokoite. A variety of chiyokoite with S^{6+} (and/or C) instead of As^{3+} may exist. Its general formula, $\text{Ca}_3(\text{Si},\text{Al})(\text{CO}_3)[\text{B}(\text{OH})_4,\text{SO}_4,\text{CO}_3](\text{OH})_6 \cdot 12\text{H}_2\text{O}$, conforms well to this end-member formula.

TABLE 5. COMPARATIVE DATA FOR CHIYOKOITE AND CHEMICALLY RELATED ETTRINGITE-GROUP MINERALS

Mineral	Chiyokoite	Imayoshiite	Thaumasite	Buryatite
Formula	$\text{Ca}_3\text{Si}(\text{CO}_3)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3\text{Si}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3(\text{Si}, \text{Fe}^{3+})(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH}, \text{O})_6 \cdot 12\text{H}_2\text{O}$
Crystal system	Hexagonal	Hexagonal	Hexagonal	Trigonal
Space group	$P6_3$	$P6_3$	$P6_3$	$P31c$ (?)
<i>a</i> (Å)	11.012	11.046	11.02–11.08	11.14
<i>c</i> (Å)	10.525	10.615	10.37–10.44	20.99
<i>V</i> (Å ³)	1105.3	1121.7	1091–1111	2256
<i>Z</i>	2	2	2	4
<i>D</i> (g/cm ³)	1.85 (meas), 1.85 (calc)	1.79 (calc)	1.84–1.89	1.89 (calc)
Strongest reflections of the powder X-ray diffraction pattern: <i>d</i> (<i>h</i>) (Å)	9.53(100) 5.50(24) 4.618(11) 3.812(23) 3.412(15) 2.726(14) 2.521(19) 2.172(13)	9.54(100) 4.636(40) 3.822(33) 2.729(31) 2.525(69) 2.174(30) 2.120(23) 1.768(28)	9.56(100) 5.51(40) 3.78(16) 3.41(20) 2.18(16) 2.713(14) 2.155(13)	9.70(80) 3.85(60) 3.04(80) 2.736(60) 2.596(100) 2.374(60) 2.121(90) 1.498(70)
References	This work	Nishio-Hamane <i>et al.</i> (2015)	Anthony <i>et al.</i> (1995); Jacobsen <i>et al.</i> (2003); Martucci & Cruciani (2006)	Malinko <i>et al.</i> (2001)

ACKNOWLEDGMENTS

We thank Herta Effenberger and an anonymous referee for their valuable comments. A part of this work (IR spectroscopic study and preliminary semi-quantitative EDS measurements) was carried out in accordance with the state task, state registration No. AAAA-A19-119092390076-7. Support by the SPbSU X-Ray Diffraction Resource Centre is acknowledged.

REFERENCES

- ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W., & NICHOLS, M.C. (1995) *Handbook of Mineralogy. Volume II. Silica, Silicates*. Mineral Data Publishing, Tucson, Arizona, United States.
- CHUKANOV, N.V. (2014) *Infrared spectra of mineral species: Extended library*. Springer Netherlands, Dordrecht, Netherlands.
- CHUKANOV, N.V. & CHERVONNYI, A.D. (2016) *Infrared Spectroscopy of Minerals and Related Compounds*. Springer International Publishing, Cham, Switzerland.
- CHUKANOV, N.V. & VIGASINA, M.F. (2020) *Vibrational (Infrared and Raman) Spectra of Minerals and Related Compounds*. Springer International Publishing, Cham, Switzerland.
- CHUKANOV, N.V., BRITVIN, S.N., VAN, K.V., MÖCKEL, S., & ZADOV, A.E. (2012) Kottenheimite, $\text{Ca}_3\text{Si}(\text{SO}_4)_2(\text{OH})_6 \cdot 12\text{H}_2\text{O}$, a new ettringite-group mineral from the Eifel area, Germany. *Canadian Mineralogist* **50**, 55–63.
- CHUKANOV, N.V., KASATKIN, A.V., ZUBKOVA, N.V., BRITVIN, S.N., PAUTOV, L.A., PEKOV, I.V., VARLAMOV, D.A., BYCHKOVA, Y.V., LOSKUTOV, A.B., & NOVGORODOVA, E.A. (2016) Tatarinovite $\text{Ca}_3\text{Al}(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$, a new ettringite-group mineral from the Bazhenovskoe deposit, Middle Urals, Russia, and its crystal structure. *Geology of Ore Deposits* **58**(8), 653–665.
- CHUKANOV, N.V., ZUBKOVA, N.V., PAUTOV, L.A., GÖTTLICHER, J., KASATKIN, A.V., VAN, K.V., KSENOFONTOV, D.A., PEKOV, I.V., VOZCHIKOVA, S.A., & PUSHCHAROVSKY, D.YU. (2019) Jouravskite: Refined data on the crystal structure, chemical composition and spectroscopic properties. *Physics and Chemistry of Minerals* **46**, 417–425.
- EDGE, A. & TAYLOR, H.F.W. (1971) Crystal structure of thaumasite $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}](\text{SO}_4)(\text{CO}_3)$. *Acta Crystallographica* **27**, 594–601.
- EFFENBERGER, H., KIRFEL, A., WILL, G., & ZOBETZ, E. (1983) A further refinement of the crystal structure of thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O}$. *Neues Jahrbuch für Mineralogie - Monatshefte*, 60–68.
- GRANGER, M.M. & PROTAS, J. (1969) Détermination et étude de la structure cristalline de la jouravskite $\text{Ca}_3\text{Mn}^{\text{IV}}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$. *Acta Crystallographica* **25**, 1943–1951.
- HENMI, C. (1995) Kusachiite, CuBi_2O_4 , a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine* **59**, 545–548.
- HENMI, C. & KUSACHI, I. (1992) Clinotobermorite, $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18} \cdot 5\text{H}_2\text{O}$, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine* **56**, 353–358.
- HENMI, C., KUSACHI, I., HENMI, K., SABINE, P.A., & YOUNG, B.R. (1973) A new mineral bicchulite, the natural analogue of gehlenite hydrate, from Fuka, Okayama Prefecture, Japan and Carneal, County Antrim, Northern Ireland. *Mineralogical Journal* **7**, 243–251.
- HENMI, C., KUSACHI, I., KAWAHARA, A., & HENMI, K. (1977) Fukalite, a new calcium carbonate silicate hydrate mineral. *Mineralogical Journal of Japan* **8**, 374–381.
- HENMI, C., KUSACHI, I., & HENMI, K. (1995) Morimotoite, $\text{Ca}_3\text{TiFe}^{2+}\text{Si}_3\text{O}_{12}$, a new titanian garnet from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine* **59**, 115–120.
- JACOBSEN, S.D., SMYTH, J.R., & SWOPE, R.J. (2003) Thermal expansion of hydrated six-coordinate silicon in thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$. *Physics and Chemistry of Minerals* **30**, 321–329.
- JUROSZEK, R., KRÜGER, B., GALUSKINA, I., KRÜGER, H., VAPNIK, Y., & GALUSKIN, E. (2020) Siwaqaite, $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, a new mineral of the ettringite group from the pyrometamorphic Daba-Siwaqa complex, Jordan. *American Mineralogist* **105**(3), 409–421.
- KUSACHI, I., HENMI, C., & HENMI, K. (1980) 10Å Tobermorite from Fuka, the Town of Bitchu, Okayama Prefecture. *Journal of the Mineralogical Society of Japan* **14**(5), 314–322 (in Japanese).
- KUSACHI, I., HENMI, C., & KOBAYASHI, S. (1995) Takedaite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine* **59**, 549–552.
- KUSACHI, I., TAKECHI, Y., HENMI, C., & KOBAYASHI, S. (1998) Parasilbirkite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine* **62**, 521–525.
- KUSACHI, I., KOBAYASHI, S., HENMI, C., & TAKECHI, Y. (1999) Calcium borate minerals in the $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system at Fuka, Okayama Prefecture, Japan. *Journal of the Mineralogical Society of Japan* **28**, 41–46 (in Japanese with English abstract).
- MALINKO, S.V., CHUKANOV, N.V., DUBINCHUK, V.T., ZADOV, A.E., & KOPORULINA, E.V. (2001) Buryatite $\text{Ca}_3(\text{Si}, \text{Fe}^{3+}, \text{Al})[\text{SO}_4][\text{B}(\text{OH})_4](\text{OH})_5 \cdot 12\text{H}_2\text{O}$, a new mineral. *Zapiski Rossiiskogo Mineralogicheskogo Obshchestva* **130**(2), 72–78 (in Russian).
- MARTUCCI, A. & CRUCIANI, G. (2006) *In situ* time resolved synchrotron powder diffraction study of thaumasite. *Physics and Chemistry of Minerals* **33**, 723–731.
- NESPOLO, M. & FERRARIS, G. (2000) Twinning by syngonic and metric merohedry. Analysis, classification and effects

- on the diffraction pattern. *Zeitschrift für Kristallographie* **215**, 77–81.
- NISHIO-HAMANE, D., OHNISHI, M., MOMMA, K., SHIMOBAYASHI, N., MIYAWAKI, R., MINAKAWA, T., & INABA, S. (2015) Imayoshiite, $\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$, a new mineral of the ettringite group from Ise City, Mie Prefecture, Japan. *Mineralogical Magazine* **79**, 413–423.
- PEKOV, I.V., CHUKANOV, N.V., BRITVIN, S.N., KABALOV, YU.K., GOTTLICHER, J., YAPASKURT, V.O., ZADOV, A.E., KRIVOVICHEV, S.V., SCHULLER, W., & TERNES, B. (2012) The sulfite anion in ettringite-group minerals: A new mineral species hielscherite, $\text{Ca}_3\text{Si}(\text{SO}_4)(\text{SO}_3)(\text{OH})_6 \cdot 11\text{H}_2\text{O}$, and the thaumasite–hielscherite solid-solution series. *Mineralogical Magazine* **76**, 1133–1152.
- PUSHCHAROVSKY, D.YU., LEBEDEVA, YU.S., ZUBKOVA, N.V., PASERO, M., BELLEZZA, M., MERLINO, S., & CHUKANOV, N.V. (2004) Crystal structure of sturmanite. *Canadian Mineralogist* **42**, 723–729.
- SHELDICK, G.M. (2015) Crystal structure refinement with *SHELXL*. *Acta Crystallographica* **C71**, 3–8.
- ZEMANN, J. & ZOBETZ, E. (1981) Do the carbonate groups in thaumasite have anomalously large deviations from coplanarity? *Soviet Physics Crystallography* **26**, 689–690.

Received April 1, 2020. Revised manuscript accepted June 9, 2020.