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Article

New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XV. Calciojohillerite, $NaCaMgMg_2(AsO_4)_3$, a member of the alluaudite group

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Abstract

The new alluaudite-group mineral calciojohillerite is one of the major arsenates in sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. In middle zones of the fumarole, calciojohillerite is associated with hematite, tenorite, johillerite, nickenichite, bradaczekite, badalovite, tilasite, lammerite, ericlaxmanite, aphthitalite-group sulfates, langbeinite, calciolangbeinite, anhydrite, sanidine, fluorophlogopite, fluoborite, cassiterite, pseudobrookite, rutile, sylvite and halite. In deep zones it occurs in association with anhydrite, diopside, hematite, svabite, berzeliite, schäferite, forsterite, magnesioferrite, ludwigite, rhabdoborite-group fluoroborates, powellite, baryte, fluorapatite, udinaite, arsenudinaite and paraberzeliite. Calciojohillerite forms prismatic crystals up to 1 cm long, their aggregates and crystal crusts up to $0.5\ m^2$. It is transparent, colourless, pale green, pale yellow, light blue, pale lilac or pink, with vitreous lustre. The mineral is brittle, with imperfect cleavage. The Mohs hardness is 3½. D_{calc} is $3.915\ g\ cm^{-3}$. Calciojohillerite is optically biaxial (–), $\alpha = 1.719(3)$, $\beta = \gamma = 1.732(3)$; $2V_{meas.} = 15(10)°$. Chemical composition (wt.%, electron-microprobe; holotype) is: Na_2O 7.32, K_2O 0.10, CaO 6.82, MgO 20.31, MnO 0.68, CuO 0.27, ZnO 0.02, Al_2O_3 0.56, Fe_2O_3 3.53, TiO_2 0.01, SiO_2 0.03, P_2O_5 1.25, V_2O_5 0.10, As_2O_5 58.77, SO_3 0.13, total 99.90. The empirical formula based on 12 O atoms is $(Na_{1.30}K_{0.01}Ca_{0.67}Mg_{2.78}Mn_{0.05}Cu_{0.02}Al_{0.06}Fe^{3+}_{0.24})_{\Sigma 5.13}(As_{2.83}P_{0.10}S_{0.01}V_{0.01})_{\Sigma 2.95}O_{12}$. Calciojohillerite is monoclinic, $C2/c$, $a = 11.8405(3)$, $b = 12.7836(2)$, $c = 6.69165(16)$ Å, $\beta = 112.425(3)°$, $V = 936.29(4)$ Å^3 and $Z = 4$. The crystal structure was solved from single-crystal X-ray diffraction data, $R_1 = 0.0227$. Calciojohillerite is isostructural with other alluaudite-group minerals. Its simplified crystal chemical formula is ${}^{A(1)}Ca^{A(1)'}\square^{A(2)}\square^{A(2)'}Na^{M(1)}Mg^{M(2)}Mg_2(AsO_4)_3$ ($\square$ = vacancy). The idealised formula is $NaCaMg_3(AsO_4)_3$, or, according to the nomenclature of alluaudite-group arsenates, $NaCaMgMg_2(AsO_4)_3$. Calciojohillerite is named as an analogue of johillerite $NaCu^{2+}MgMg_2(AsO_4)_3$ with species-defining Ca instead of Cu in the ideal formula.

Keywords: calciojohillerite, new mineral, alluaudite group, arsenate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka

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Introduction

Arsenates of fumarolic origin are specific and, as recent data show, numerous: more than 50 valid mineral species belonging to this chemical class are known in volcanic sublimates. All of them are hydrogen-free. The most prolific locality of these minerals is the Arsenatnaya fumarole situated at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′N 160°14′E, 1200 m a.s.l.). One of the outstanding features of this fumarole is the abundance of new arsenate minerals (Pekov *et al.*, 2018a). Seventeen new species were characterised in the previous articles of this series, namely yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al.*, 2014a), two polymorphs of $Cu_4O(AsO_4)_2$, ericlaxmanite and kozyrevskite (Pekov *et al.*, 2014b), popovite $Cu_5O_2(AsO_4)_2$ (Pekov *et al.*, 2015a), structurally related shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2015b), katiarsite $KTiO(AsO_4)$ (Pekov *et al.*, 2016a), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (Pekov *et al.*, 2016b), pharmazincite $KZnAsO_4$ (Pekov *et al.*, 2017), arsenowagnerite $Mg_2(AsO_4)F$ (Pekov *et al.*, 2018b), arsenatrotitanite $NaTiO(AsO_4)$ (Pekov *et al.*, 2019a), the two isostructural minerals edtollite $K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$ and alumoedtollite $K_2NaCu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2019b), anatolyite $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ (Pekov *et al.*, 2019c), zubkovaite $Ca_3Cu_3(AsO_4)_4$ (Pekov *et al.*, 2019d), pansnerite $K_3Na_3Fe^{3+}_6(AsO_4)_8$ (Pekov *et al.*, 2020a) and badalovite $NaNaMg(MgFe^{3+})(AsO_4)_3$

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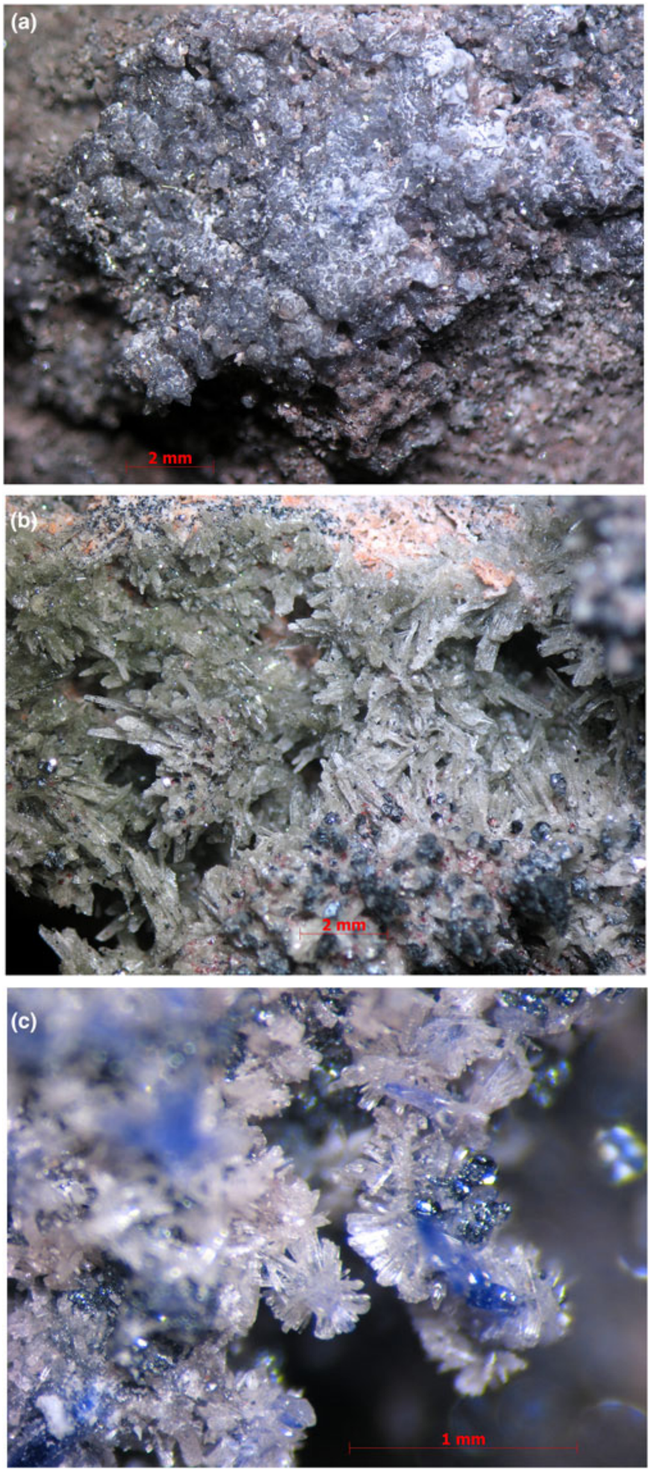

Fig. 1. Aggregates of calciojohillerite: (a, sample #4789: holotype specimen) crust of coarse short-prismatic, almost isometric colourless crystals on basalt scoria altered by fumarolic gas, (b, sample #4713) chaotic aggregates of coarse prismatic pale greenish-grey crystals with iron-black hematite on crust of As-bearing sanidine and (c, sample #4671) radial clusters of prismatic colourless to pale lilac crystals with deep blue johillerite and iron-black hematite. FOV widths: (a, b) 14.5 mm, (c) 2.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

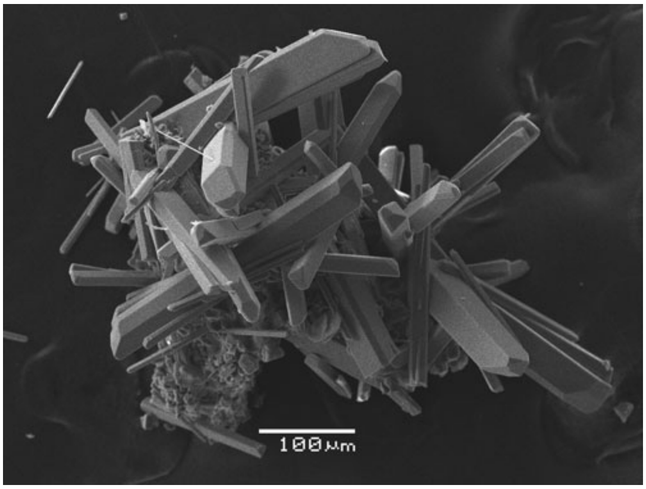

Fig. 2. Group of calciojohillerite crystals. SEM (SE mode) image.

(Pekov *et al.*, 2020b). The latter belongs to the alluaudite group, a subdivision of the alluaudite supergroup, as well as the new mineral calciojohillerite described in the present paper.

Calciojohillerite has the idealised formula $NaCaMg_3(AsO_4)_3$, or, in accordance with the nomenclature of alluaudite-group arsenates (Hatert, 2019), $NaCaMgMg_2(AsO_4)_3$. It is named as an analogue of johillerite $NaCu^{2+}MgMg_2(AsO_4)_3$ with species-defining calcium instead of copper in the ideal, end-member formula.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification, IMA2016–068 (Pekov *et al.*, 2016c). The holotype specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 95621.

Occurrence and general appearance

At present, the Arsenatnaya fumarole is the largest and one of the hottest among strongly mineralised active fumaroles related to the Tolbachik volcano. The general description of Arsenatnaya and the data on zonation in distribution of mineral parageneses in this fumarole were reported by us earlier (Pekov *et al.*, 2014a, 2018a; Shchipalkina *et al.*, 2020).

Calciojohillerite is found in all middle and deep zones of the fumarole, from the so-called polymineralic zone (depth of 1.5–2 m from the surface) to the lowest, so-called anhydrite zone (3–4 m deep). Temperatures measured by us using a chromel–alumel thermocouple at the time of collecting (in 2015–2018) in different pockets with the new mineral varied from 360–380°C (polymineralic zone) to 450–490°C (anhydrite zone). Calciojohillerite is a constituent of sublimate incrustations formed in open space in fumarole chambers and cracks, or in vesicles of basalt scoria. We believe that the mineral crystallised at temperatures not lower than 500°C. It was deposited directly from the gas phase or, more probably, formed as a result of the interaction between hot volcanic gas and basalt scoria. The latter could be a source of Mg and Ca which have very low volatilities in such post-volcanic systems (Symonds and Reed, 1993).

The first specimen, which became the holotype of calciojohillerite, was collected in July 2015 from the polymineralic zone of Arsenatnaya. The new mineral is associated here with hematite, tenorite, johillerite, nickenichite, bradaczekite, hatertite, magnesiohatertite, badalovite, aphthitalite-group sulfates, langbeinite, calciolangbeinite, sanidine (As-bearing variety), fluorophlogopite, fluoborite, tilasite, anhydrite, pseudobrookite, rutile, sylvite, halite, lammerite, lammerite-β, urusovite, ericlaxmanite, kozyrevskite,

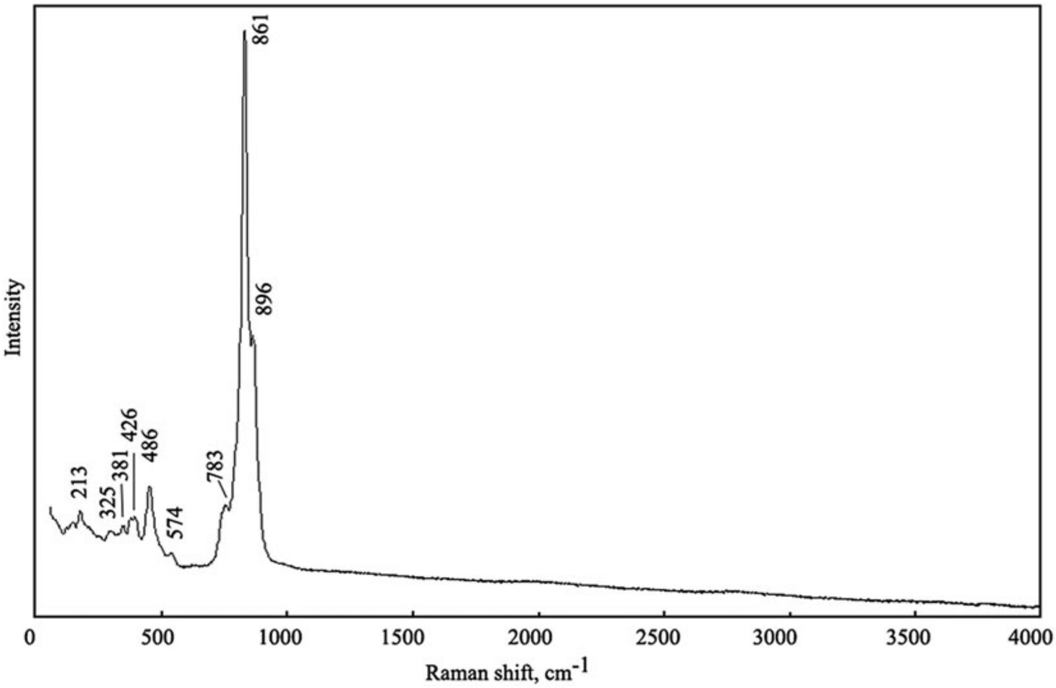

Fig. 3. The Raman spectrum of calciojohillerite.

arsmirandite, svabite, popovite, dmisokolovite, shchurovskyite, yurmarinite, krasheninnikovite, euchlorine, wulffite, alumoklyuchevskite, sellaite, gahnite and corundum. In the polymineralic zone, calciojohillerite is not a very common mineral.

Our fieldwork in 2016–2018 showed that calciojohillerite is a typical, sporadically main crust-forming mineral at deep levels of the Arsenatnaya fumarole. In the zone located at a depth of 2–3 m from the surface and intermediate between the polymineralic and anhydrite zones, calciojohillerite is the most abundant arsenate, the major concentrator of As. It forms, sometimes together with badalovite, crystal crusts up to 0.5 m^2 in area and up to 1 cm thick which cover walls of cracks and cavities. Copper minerals, so rich and diverse further up, in the polymineralic zone, are almost absent here, except for minor amounts of johillerite and nickenichite. Calciojohillerite and other alluaudite-group arsenates are typically associated in this zone with fluorophlogopite, sanidine, diopside, hematite, cassiterite, anhydrite, metathénardite, belomarinaite, sylvite, tilasite, svabite and arsenowagnerite.

In the anhydrite zone, calciojohillerite also occurs in significant amounts. It is common in sublimate incrustations (up to 3 cm thick) which mainly consist of anhydrite, diopside and hematite and sporadically contain svabite and garnets of the berzeliite–schäferite series as important crust-forming constituents. Other typical minerals here are forsterite, magnesioferrite, spinel, ludwigite, rhabdoborite-group fluoroborates, powellite, baryte, fluorapatite, wagnerite (As-bearing variety), udinaite, arsenudinaite and paraberzeliite.

Calciojohillerite occurs as prismatic crystals, usually up to 1 mm in size, rarely up to 1 mm × 2 mm × 10 mm. Sometimes the crystals are short prismatic, almost isometric (Fig. 1a), but more commonly long prismatic (Figs 1b,c and 2) to acicular or spear-like, elongated along [001]. Crystals are crude or well-shaped, in some specimens divergent. They are typically assembled in bunches, sheaf-like or radial aggregates (Fig. 1c).

Isolated crystals of calciojohillerite are rare; they commonly form chaotic groups, brushes or interrupted crusts (Figs 1 and 2) up to several cm^2, rarely up to 0.5 m^2 in area which overgrow incrustations of sanidine, fluorophlogopite, diopside and/or hematite or directly cover basalt scoria altered by fumarolic gas.

Table 1. Chemical composition of calciojohillerite.

Constituent	[1]	[2]	[3]	[4]
Wt.%				
Na_2O	7.32 (7.22–7.43)	4.76	5.72	5.61
K_2O	0.10 (0.10–0.11)	0.05	0.07	
CaO	6.82 (6.62–7.04)	11.83	10.66	10.15
MgO	20.31 (20.03–20.59)	22.51	23.02	21.87
MnO	0.68 (0.66–0.73)	0.19	0.22	
CuO	0.27 (0.16–0.43)	0.20	0.19	
ZnO	0.02 (0.00–0.03)	–	–	
Al_2O_3	0.56 (0.50–0.65)	–	–	
Fe_2O_3*	3.53 (3.38–3.77)	0.10	0.43	
TiO_2	0.01 (0.00–0.03)	–	–	
SiO_2	0.03 (0.02–0.04)	0.03	–	
P_2O_5	1.25 (1.02–1.44)	2.74	5.76	
V_2O_5	0.10 (0.08–0.13)	5.28	8.61	
As_2O_5	58.77 (57.93–59.04)	52.60	44.22	62.37
SO_3	0.13 (0.10–0.15)	0.42	0.45	
Total	99.90	100.71	99.35	100.00
Formula calculated on the basis of 12 O apfu				
Na	1.30	0.82	0.97	1
K	0.01	0.01	0.01	
Ca	0.67	1.12	1.00	1
Mg	2.78	2.97	3.00	3
Mn	0.05	0.01	0.02	
Cu	0.02	0.01	0.01	
Al	0.06	–	–	
Fe^{3+}	0.24	0.01	0.03	
P	0.10	0.21	0.43	
V	0.01	0.31	0.50	
As	2.83	2.43	2.02	3
S	0.01	0.03	0.03	

[1] Sample #4789: holotype, from polymineralic zone of the Arsenatnaya fumarole (average for five spot analyses, ranges are in parentheses); [2] sample #5358 and [3] sample #5348, both from anhydrite zone of the Arsenatnaya fumarole; [4] $NaCaMg_3(AsO_4)_3$. '–' indicates content is below the detection limit. *All Fe is considered as Fe^{3+} (see text).

Table 2. Powder X-ray diffraction data (*d* in Å) of calciojohillerite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*hkl*
3	8.31	4	8.314	110
7	6.398	18	6.392	020
5	5.471	11	5.473	200
6	4.387	4, 26	4.445, 4.391	021, 111
7	4.156	6	4.157	220
10	4.033	32	4.034	$\bar{2}21$
5	3.687	20	3.687	$\bar{3}11$
9	3.576	32	3.574	$\bar{1}31$
16	**3.509**	29	3.508	310
3	3.283	2	3.282	$\bar{2}02$
19	**3.220**	47, 5	3.220, 3.196	$\bar{1}12$, 040
3	3.149	9	3.149	131
6	3.062	15	3.064	221
17	**2.910**	12, 33	2.919, 2.909	$\bar{2}22$, $\bar{3}12$
7	2.840	17	2.839	041
100	**2.758**	100	2.760	240
25	**2.735**	37	2.736	400
7	2.681	10	2.681	$\bar{4}21$
8	2.654	25	2.658	112
12	**2.620**	42	2.622	$\bar{1}32$
6	2.597	10	2.600	$\bar{4}02$
6	2.514	5	2.515	420
4	2.320	4	2.327	$\bar{5}11$
5	2.287	6, 4	2.293, 2.291	331, 132
9	2.152	10, 1	2.158, 2.131	510, 060
7	2.090	9	2.094	350
5	2.010	5	2.014	061
8	1.974	17, 4	1.978, 1.969	$\bar{5}32$, $\bar{4}23$
10	1.940	4, 13	1.943, 1.942	$\bar{1}33$, $\bar{3}52$
3	1.875	3, 5	1.878, 1.878	113, $\bar{6}21$
3	1.859	10	1.862	152
6	1.815	17	1.819	261
3	1.757	7	1.759	$\bar{1}71$
3	1.726	5	1.728	$\bar{4}61$
16	**1.661**	26, 6, 2, 1	1.663, 1.663, 1.662, 1.661	$\bar{2}04$, 550, $\bar{7}12$, $\bar{7}11$
4	1.646	12	1.649	$\bar{6}42$
11	**1.582**	16	1.584	640
8	1.550	12, 1, 4, 1, 2	1.558, 1.555, 1.552, 1.547, 1.545	$\bar{3}72$, $\bar{7}13$, 710, 081, 621
3	1.527	5, 5, 4	1.532, 1.527, 1.521	442, $\bar{2}81$, 512
8	1.515	3, 8, 11	1.518, 1.516, 1.516	243, 371, 172
5	1.467	3, 6	1.470, 1.468	$\bar{7}33$, 730
7	1.458	13, 4	1.460, 1.453	$\bar{4}44$, 281
5	1.400	3, 3, 4, 6	1.402, 1.402, 1.402, 1.401	570, $\bar{3}73$, $\bar{7}52$, $\bar{1}73$

*For the calculated pattern, only reflections with intensities ≥1 are given; **for the unit-cell parameters calculated from single-crystal data; the strongest reflections are marked in bold type.

Physical properties and optical data

Calciojohillerite is transparent, typically colourless, pale green, pale yellow or light blue, sometimes pale lilac, pink, bluish-, greenish- or yellowish-grey. The streak is white and lustre is vitreous. The mineral is brittle. One direction of imperfect cleavage was observed under the microscope; parting was not observed. The fracture is uneven. The Mohs hardness is *ca.* 3½. Density calculated for the holotype using the empirical formula is 3.915 g cm^{-3}.

In plane polarised transmitted light, calciojohillerite is colourless and non-pleochroic. It is optically biaxial (–), $\alpha = 1.719(3)$, $\beta = \gamma = 1.732(3)$ (589 nm); $2V_{meas.} = 15(10)°$ (estimated by the curve of the conoscopic figures on the sections perpendicular to the acute bisectrix), $2V_{calc.} = 0°$. Dispersion of optical axes is medium, $r > v$. Optical orientation: $Y = b$.

Raman spectroscopy

The Raman spectrum of the holotype calciojohillerite (Fig. 3) was obtained on a randomly oriented crystal using an EnSpectr R532 instrument with a green laser (532 nm) at room temperature. The output power of the laser beam was ~16 mW. The spectrum was processed using the *EnSpectr* expert mode program in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 lines per cm and a resolution of 6 cm^{-1}. The diameter of the focal spot on the sample was ~10 µm. The back-scattered Raman signal was collected with a 40× objective; signal acquisition time for a single scan of the spectral range was 1500 ms and the signal was averaged over 20 scans.

The strongest bands in the region 750–950 cm^{-1} in the Raman spectrum of calciojohillerite correspond to As^{5+}–O stretching vibrations of AsO_4^{3-} anions. A weak band with a maximum at 574 cm^{-1} probably corresponds to Fe^{3+}–O stretching vibrations caused by admixed Fe^{3+} in the holotype specimen. Bands with frequencies lower than 500 cm^{-1} correspond to bending vibrations of AsO_4 tetrahedra, Mg–O, Ca–O and Na–O stretching vibrations and lattice modes. The bands in the spectrum are assigned according to Nakamoto (1986). The absence of bands with frequencies higher than 950 cm^{-1} indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds in the mineral.

Table 3. Crystal data, data collection information and structure refinement details for calciojohillerite.

Crystal data	
Formula	$^{A(2)'}(Na_{0.99}K_{0.01})\ ^{A(1)}(Ca_{0.70}Na_{0.25})\ ^{A(1)'}Cu_{0.02}\ ^{M(1)}(Mg_{0.95}Mn_{0.05})\ ^{M(2)}(Mg_{1.70}Fe_{0.25}Al_{0.05})(As_{2.85}P_{0.15})O_{12}$
Formula weight	550.87
Temperature (K)	293(2)
Radiation and wavelength (Å)	Mo*K*α; 0.71073
Crystal system, space group, *Z*	Monoclinic, *C*2/*c*, 4
Unit cell dimensions (Å, °)	$a = 11.8405(3)$, $b = 12.7836(2)$, $c = 6.69165(16)$, $\beta = 112.425(3)$
V (Å^3)	936.29(4)
Absorption coefficient, μ (mm^{-1})	11.326
F_{000}	1044
Data collection	
Crystal size (mm)	0.07 × 0.13 × 0.14
Diffractometer	Xcalibur S CCD
θ range for data collection (°)	3.187–34.818
Index ranges	$-18 \le h \le 18$, $-19 \le k \le 19$, $-10 \le l \le 10$
Reflections collected	11,990
Independent reflections	1947 ($R_{int} = 0.0455$)
Independent reflections with $I > 2\sigma(I)$	1825
Refinement	
Data reduction	*CrysAlisPro*, version 1.171.37.35 (Agilent Technologies, 2014)
Absorption correction	Gaussian [numerical absorption correction based on Gaussian integration over a multifaceted crystal model]
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	101
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0227$, $wR_2 = 0.0453$
R indices (all data)	$R_1 = 0.0255$, $wR_2 = 0.0465$
GoF	1.056
Largest diff. peak and hole (e^-/Å^3)	0.72 and –0.57

Chemical composition

The chemical composition of calciojohillerite was determined with a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a 10 μm beam diameter. The following standards were used: jadeite (Na, Al and Si), $KTiOPO_4$ (K, Ti and P), wollastonite (Ca), olivine (Mg), $MnTiO_3$ (Mn), Cu (Cu), ZnS (Zn, S), FeS_2 (Fe), V (V) and GaAs (As). Contents of other elements with atomic numbers higher than carbon are below detection limits. H_2O was not analysed because both structure data and Raman spectrum show its absence.

The empirical formula of the holotype specimen (Table 1, #1) calculated on the basis of 12 O atoms per formula unit (apfu) is $(Na_{1.30}K_{0.01}Ca_{0.67}Mg_{2.78}Mn_{0.05}Cu_{0.02}Al_{0.06}Fe^{3+}_{0.24})_{\Sigma 5.13}(As_{2.83}P_{0.10}S_{0.01}V_{0.01})_{\Sigma 2.95}O_{12}$. In comparison with the holotype originated from the polymineralic zone of the Arsenatnaya fumarole, calciojohillerite from the anhydrite zone contains much less admixed Fe but is enriched with V and P, which both substitute As (Table 1, ##2–3).

Table 5. Refined site-scattering factors and assignment for cation sites *A* and *M* in the structure of calciojohillerite.

Site	SC	s.o.f.	SSF_{exp} (e^-)	Assigned occupancy	SSF_{calc} (e^-)
A(1)	Ca	0.80	16.00	$Ca_{0.70}Na_{0.25}$	16.75
A(2)'	Na	0.98	10.78	$Na_{0.99}K_{0.01}$	11.08
M(1)	Mg	1.02	12.24	$Mg_{0.95}Mn_{0.05}$	12.65
M(2)	Mg	1.18	14.16	$Mg_{0.85}Fe_{0.125}Al_{0.025}$	13.78

SC – scattering curve used for refinement of site occupancy, s.o.f – refined site occupancy factor, SSF_{exp} and SSF_{calc} – experimental and calculated site-scattering factors, respectively.

X-ray crystallography and crystal structure determination

Powder X-ray diffraction data (XRD) of the holotype calciojohillerite (Table 2) were obtained with a DRON-2 diffractometer using Cu*K*α radiation. Parameters of the monoclinic unit cell calculated from the powder XRD data are: $a = 11.83(1)$, $b = 12.772(5)$, $c = 6.686(8)$ Å, $\beta = 112.41(8)°$ and $V = 934(2)$ Å^3.

Single-crystal XRD studies of the holotype calciojohillerite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Intensity data were corrected for Lorentz and polarisation effects. Calciojohillerite is a monoclinic mineral which crystallises in the space group *C*2/*c*; unit-cell parameters are:

Table 4. Coordinates and equivalent displacement parameters (U_{eq}, in Å^2) of atoms, bond-valence sums (BVS) and site multiplicities (*Q*) for calciojohillerite.

Site	*x*	*y*	*z*	U_{eq}	BVS*	*Q*
A(1)	½	0	0	0.0192(3)	1.64	4
A(1)'**	0	0.5027(13)	¼	0.006(3)***	0.04	4
A(2)'	0	–0.00980(14)	¼	0.0261(5)	0.89	4
M(1)	0	0.26340(7)	¼	0.0076(3)	1.89	4
M(2)	0.28625(5)	0.65740(4)	0.37724(9)	0.00519(16)	2.24	8
As(1)	0	0.71086(2)	¼	0.00595(7)	4.95	4
As(2)	0.23151(2)	0.88687(2)	0.12070(3)	0.00563(6)	4.97	8
O(1)	0.46311(13)	0.71706(11)	0.5239(2)	0.0101(3)	1.95	8
O(2)	0.10889(14)	0.62355(12)	0.2629(3)	0.0150(3)	2.02	8
O(3)	0.34097(13)	0.67044(11)	0.1214(2)	0.0096(3)	1.94	8
O(4)	0.11777(13)	0.39710(11)	0.3199(2)	0.0111(3)	1.99	8
O(5)	0.21645(14)	0.81611(11)	0.3204(2)	0.0106(3)	1.91	8
O(6)	0.33719(14)	0.50319(11)	0.3958(2)	0.0114(3)	1.98	8

*Bond-valence parameters are taken from (Brese and O'Keeffe, 1991). All calculations were done taking into account the cation distribution shown in Table 5. **The *A*(1)' site was localised from a difference-Fourier synthesis and could contain a small amount of Cu^{2+}, as is typical for other Cu-bearing alluaudite-group arsenates (see text). ***U_{iso}.

Table 6. Selected interatomic distances (Å) in the structure of calciojohillerite.

A(1)–O(2)	2.3499(15) ×2	*A*(2)'–O(6)	2.4196(16) ×2
A(1)–O(4)	2.4454(15) ×2	*A*(2)'–O(6)	2.4762(15) ×2
A(1)–O(4)	2.5317(15) ×2	*A*(2)'–O(3)	2.891(2) ×2
A(1)–O(2)	2.8694(17) ×2	*A*(2)'–O(1)	2.999(2) ×2
<*A*(1)–O>	2.549	<*A*(2)'–O>	2.697
A(1)'–O(4)	1.868(12) ×2	*M*(2)–O(2)	1.9892(17)
A(1)'–O(2)	1.992(13) ×2	*M*(2)–O(6)	2.0513(15)
<*A*(1)'–O>	1.930	*M*(2)–O(3)	2.0553(15)
		M(2)–O(5)	2.0640(15)
M(1)–O(3)	2.1124(15) ×2	*M*(2)–O(1)	2.0886(16)
M(1)–O(1)	2.1241(14) ×2	*M*(2)–O(5)	2.1690(16)
M(1)–O(4)	2.1416(16) ×2	<*M*(2)–O>	2.070
<*M*(1)–O>	2.126		
As(1)–O(1)	1.6807(14) ×2	As(2)–O(5)	1.6783(14)
As(1)–O(2)	1.6823(15) ×2	As(2)–O(6)	1.6783(14)
<As(1)–O>	1.682	As(2)–O(4)	1.6789(14)
		As(2)–O(3)	1.6845(14)
		<As(2)–O>	1.680

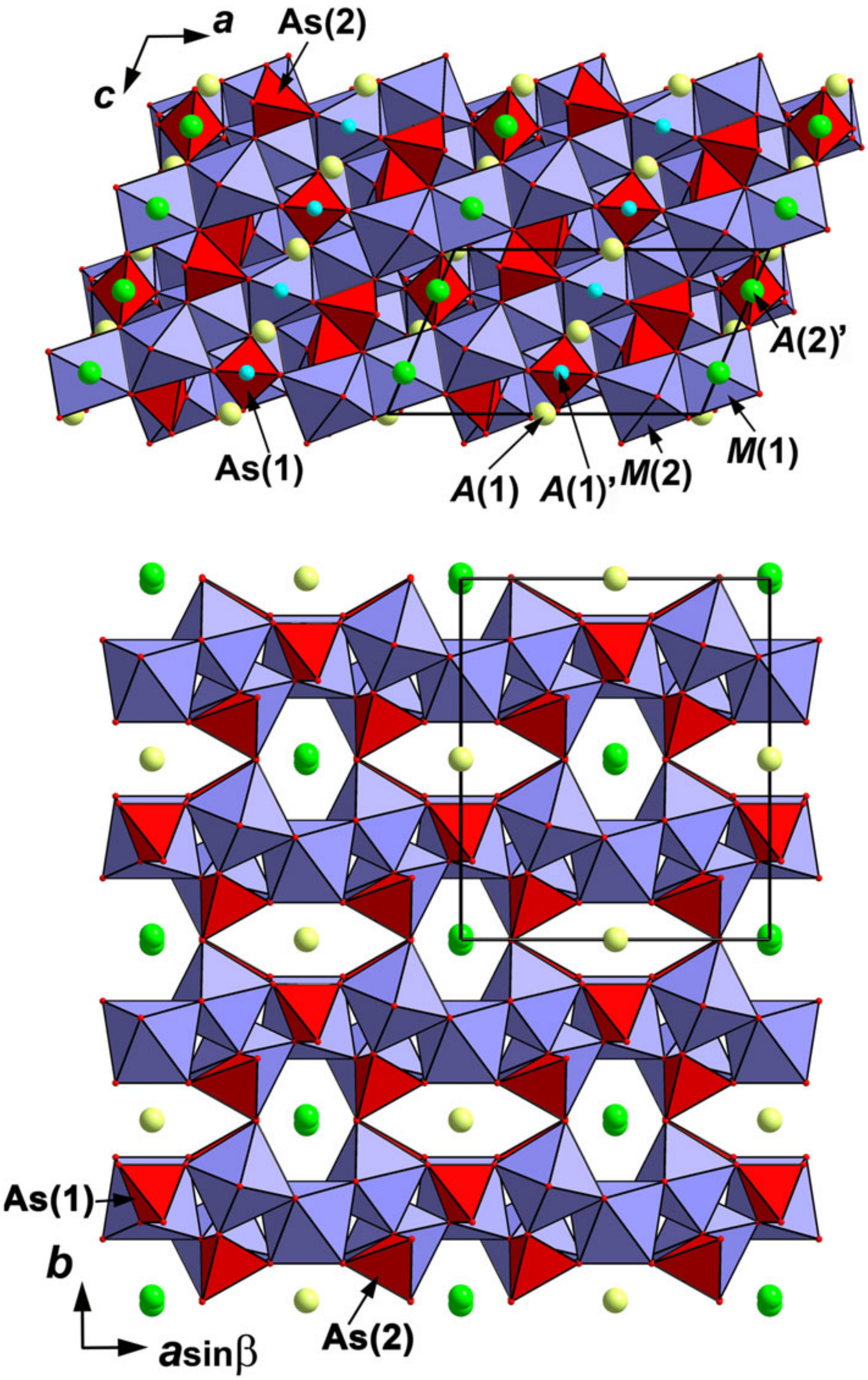

Fig. 4. The crystal structure of calciojohillerite in two projections: along the *b* axis (the upper drawing) and along the *c* axis (the lower drawing). As-centred tetrahedra are red, *M*-centred octahedra are purple, *A*(1), *A*(1)' and *A*(2)' sites are given as yellow, blue and green circles, respectively. The unit cell is outlined.

$a = 11.8405(3)$, $b = 12.7836(2)$, $c = 6.69165(16)$ Å, $\beta = 112.425(3)°$, $V = 936.29(4)$ Å^3 and $Z = 4$. The unit-cell data obtained from single-crystal and powder XRD data are in a good agreement. The crystal structure of the new mineral was solved by direct methods and refined using the *SHELX-97* software package (Sheldrick, 2008) to $R_1 = 0.0227$ on the basis of 1825 independent reflections with $I > 2\sigma(I)$. Crystal data, data collection information and structure refinement details are given in Table 3, coordinates and thermal displacement parameters of atoms and bond-valence sums in Table 4, refined site-scattering factors and assigned occupancies for mixed-occupied metal cation sites *A* and *M* in Table 5 and selected interatomic distances in Table 6. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Discussion

The alluaudite supergroup includes monoclinic phosphate and arsenate minerals with the general formula $A(2)'A(1)M(1)M(2)_2(T^{5+}O_4)_3$ in which T^{5+} = P or As, whereas *A* and *M* are cations which occupy sites ranked in descending order of the size. The *M* sites are fully occupied while the *A* sites can be empty or partially occupied (Jebli *et al.*, 2016; Hatert, 2019). The alluaudite group forms the major part of the alluaudite supergroup. In particular, all 20 alluaudite-supergroup arsenates known to date belong to the alluaudite group. The species-defining *M* and *A* components known in alluaudite-group arsenates are as follows: M = Mg, Mn^{2+}, Fe^{3+}, Cu^{2+}, Zn, Cd, Ca or Na; A = Na, Ca, Cu^{2+} or vacancy; some of these minerals are H-bearing, i.e. contain acidic arsenate anions or H_2O (Hatert, 2019).

The crystal structure of calciojohillerite (Fig. 4) is typical for a member of the alluaudite group (Moore and Ito, 1979; Krivovichev *et al.*, 2013; Hatert, 2019 and references therein). It contains zig-zag chains of edge-sharing $M(1)O_6$ and $M(2)O_6$ octahedra; in calciojohillerite M = Mg (with admixtures of Fe^{3+}, Al and Mn in the holotype). The octahedral chains consist of $[M(2)_2O_{10}]$ dimers of the $M(2)O_6$ octahedra connected *via* isolated $M(1)O_6$ octahedra. Arsenic atoms occupy two crystallographically independent tetrahedrally coordinated sites. In both sites As is partially substituted by P; in accordance with electron-microprobe data, the As:P ratio in the sites was fixed as $As_{0.95}P_{0.05}$. $As1O_4$ tetrahedra share all vertices with the *M*-centred octahedra forming (010) heteropolyhedral layers while each $As(2)O_4$ tetrahedron shares three vertices with the MO_6 octahedra of one layer and the fourth vertex with the octahedron of the adjacent layer, thus linking the layers to a three-dimensional framework (Fig. 4). The framework contains channels of two types in which the *A* sites are located. The *A*(1) site is coordinated by six O atoms with the distances in the range from 2.3500(16) to 2.5315(16) Å; two elongated *A*(1)–O(2) bonds [2.8695(18) Å] could also be included in the coordination sphere of *A*(1). The *A*(1) site is occupied by Ca with admixed Na (Tables 4 and 5). A small amount of Cu revealed by electron microprobe (Table 1) could be localised in the *A*(1)' site (see below) found in the difference-Fourier synthesis. The *A*(1)' site has square planar oxygen coordination with *A*(1)'–O distances varying from 1.87 to 1.99 Å. The *A*(1) and *A*(1)' sites alternate in rows parallel to [001] with a formal *A*(1)–*A*(1)' distance of 1.673 Å; thus, the neighbouring sites within one channel cannot be occupied simultaneously. If minor Cu (0.02 apfu) is located in *A*(1)' then the *A*(1) site should be partially (at least for 2%) vacant. The *A*(2)' site in calciojohillerite is occupied by Na, probably with traces of K, and centres an eight-fold polyhedron with *A*(2)'–O distances in the range from 2.419(2) to 2.999(2) Å (Table 6).

The presence of admixed Fe in trivalent state in the holotype calciojohillerite is confirmed by the bond-valence sum for *M*(2) (2.24 valence units: Table 4) and is in agreement with extremely oxidising conditions of mineral deposition in the Arsenatnaya fumarole: all other iron-bearing minerals, known from here, contain only Fe^{3+} (Pekov *et al.*, 2018a; Shchipalkina *et al.*, 2020).

Synthetic $NaCaMg_3(AsO_4)_3$, an analogue of the end-member calciojohillerite, demonstrates in general, the same distribution of cations as the mineral, with only slight differences in the content of the *A* sites: $(Na_{0.7}Ca_{0.3})$ in *A*(2)' and $(Ca_{0.7}Na_{0.3})$ in *A*(1) (Abdallah and Haddad, 2008).

Table 7. Comparative data for arsenate minerals of the alluaudite group with Mg prevailing in both *M*(1) and *M*(2) sites.

Mineral	Calciojohillerite	Johillerite	Nickenichite
Simplified formula	$NaCaMg_3(AsO_4)_3$	$NaCuMg_3(AsO_4)_3$	$Na(Ca_{0.5}Cu_{0.5})Mg_3(AsO_4)_3$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c**	*C*2/*c*
a (Å)	11.841	11.86–11.91	11.882
b (Å)	12.784	12.73–12.76	12.760
c (Å)	6.692	6.70–6.77	6.647
β (Å)	112.43	113.0–113.6	112.81
V ($Å^3$)	936.3	932–936	929.0
Z	4	4	4
Species-defining constituents at the *A* sites**:			
A(1)	Ca	$\square$	$(\square_{0.5}Ca_{0.5})$
A(1)'	$\square$	Cu	$(\square_{0.5}Cu_{0.5})$
A(2)'	Na	Na	Na
D_{calc} (g cm^{-3})	3.915	4.17–4.30	4.06
Strongest reflections of the powder X-ray diffraction pattern: *d* (Å) – *I*	3.509–16 3.220–19 2.910–17 2.758–100 2.735–25 2.620–12 1.661–16 1.582–11	4.06–50 3.50–40 3.25–80 2.75–100 2.64–50 1.952–40 1.660–50	4.35–30 4.06–30 3.56–30 3.53–30 3.195–40 3.066–30 2.744–100 2.605–30
Optical data:			
α	1.719	1.715	1.714
β	1.732	1.743	1.744
γ	1.732	1.783	1.783
Birefringence	0.013	0.068	0.069
Optical sign, 2V (meas)	–15°	+80°	+60°
References	This work	Keller *et al.* (1982); Keller and Hess (1988); Tait and Hawthorne (2004); Koshlyakova *et al.* (2018)	Auernhammer *et al.* (1993)

*Tait and Hawthorne (2004) presented the crystal structure of johillerite in the space group *I*2/*a* with unit-cell parameters: *a* = 6.752, *b* = 12.739, *c* = 11.068 Å and β = 100.37°; here this setting is given transformed to the standard setting (*C*2/*c*) for better comparison with other alluaudite-group arsenates.

**The sites *A*(1)'', *A*(2) and *A*(2)'' vacant in all three minerals are not included.

Only three alluaudite-group arsenate minerals are characterised by Mg predominance at both *M*(1) and *M*(2) sites, i.e., have 3 apfu Mg in the idealised formula, namely johillerite $NaCuMg_3(AsO_4)_3$, calciojohillerite $NaCaMg_3(AsO_4)_3$ and nickenichite $Na(Ca_{0.5}Cu_{0.5})Mg_3(AsO_4)_3$ (Hatert, 2019). They differ from each other in species-defining constituents at positions belonging to the *A*1 group (Table 7) which includes three closely located sites labelled as *A*(1), *A*(1)' and *A*(1)''. Only one of them can have more than 50% occupancy due to a short cation–cation distance: <2 Å. The *A*(1)'-centred polyhedron is the smallest and has flat-square oxygen coordination and only the cation, Cu^{2+}, is known to be located there in arsenate minerals of the group, with *A*(1)'–O distances lying in the range from 1.82 to 1.99 Å (Keller and Hess, 1988; Auernhammer *et al.*, 1993; Krivovichev *et al.*, 2001; Tait and Hawthorne, 2004; Malcherek and Schlüter, 2013; Schlüter *et al.*, 2013; Koshlyakova *et al.*, 2018; Pekov *et al.*, 2020c). This is in a good agreement with the ionic radius of Cu^{2+} and with a strong tendency of Cu^{2+}-centred polyhedra for the Jahn–Teller distortion. Both *A*(1) and *A*(1)'' are large-cation sites: eight-coordinated *A*(1) with *A*(1)–O distances from 2.32 to 3.06 Å [or six-coordinated in the case of hatertite with *A*(1)–O distances from 2.31 to 2.61 Å and two strongly elongated distances (3.22 Å) not included in the coordination sphere of *A*(1): Krivovichev *et al.*, 2013] and seven-coordinated *A*(1)'' with *A*(1)''–O from 2.34 to 2.83 Å. They are occupied by Na or Ca in all arsenate minerals of the alluaudite group (Hatert, 2019 and references therein).

Johillerite $^{A(2)'}Na[^{A(1)}\square^{A(1)'}Cu^{A(1)''}\square]^{M(1)}Mg^{M(2)}Mg_2(^{T}AsO_4)_3$, calciojohillerite $^{A(2)'}Na[^{A(1)}Ca^{A(1)'}\square^{A(1)''}\square]^{M(1)}Mg^{M(2)}Mg_2(^{T}AsO_4)_3$ and nickenichite $^{A(2)'}Na[^{A(1)}(\square_{0.5}Ca_{0.5})^{A(1)'}(\square_{0.5}Cu_{0.5})^{A(1)''}\square]^{M(1)}Mg^{M(2)}Mg_2(^{T}AsO_4)_3$ thus demonstrate three different cases of content and, correspondingly, different distribution of species-defining constituents in positions of the *A*1 group (Hatert, 2019).

Typical calciojohillerite is almost Cu-free (Table 1; see also Pekov *et al.*, 2018a), which is reflected in its properties. Unlike johillerite and nickenichite which are usually bright or deep blue or violet, it is colourless or has pale colour (Fig. 1). Calciojohillerite also differs distinctly from johillerite and nickenichite in optical data, especially in optical sign and birefringence (Table 7).

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