

## A New Chladniite Variety from Volcanic Exhalations. The Genetic Crystal Chemistry of Chladniite

Corresponding Member of the RAS I. V. Pekov<sup>a,\*</sup>, N. V. Zubkova<sup>a</sup>, A. A. Agakhanov<sup>b</sup>, A. G. Turchkova<sup>a</sup>,  
E. S. Zhitova<sup>c</sup>, and Academician D. Yu. Pushcharovskii<sup>a</sup>

Received June 20, 2023; revised June 26, 2023; accepted July 4, 2023

**Abstract**—A new, unusual, Fe-free, and As<sup>5+</sup>-rich variety of chladniite, a rare phosphate of the fillowite group, was found in exhalations of the active Arsenatnaya fumarole, Tolbachik Volcano, Kamchatka, Russia. It belongs to the high-temperature (500–750°C) paragenesis with calciojohillerite, fluorapatite, metathénardite, diopside, enstatite, forsterite, and hematite. This genetic type is novel for fillowite-group minerals. The crystal structure of Tolbachik chladniite is determined,  $R1 = 4.32\%$ . It is trigonal,  $R-3$ ,  $a = 14.9831(2)$  Å,  $c = 42.8050(7)$  Å, and  $V = 8322.1(3)$  Å<sup>3</sup>. The structural formula is  $M^{13}(\text{Na}_{0.56}\square_{0.44})_2^{M^{21}}(\text{Na}_{0.81}\text{Ca}_{0.19})_2^{M^{31}}(\text{Na}_{0.97}\square_{0.03})_6^{M^{12}}(\text{Ca}_{0.64}\text{Na}_{0.36})_6^{M^1}\text{Mn}^{M^2}(\text{Mg}_{0.54}\text{Ca}_{0.46})^{M^{3-9}}\text{Mg}_{30}^{M^{10}}(\text{Mg}_{0.94}\text{Ca}_{0.06})_6^{M^{11}}\text{Mg}_6(\text{P}_{33.53}\text{As}_{2.47})\text{O}_{144}$  ( $Z = 3$ ). The crystal chemical features of chladniite and their correlation with formation settings are discussed for all chladniite findings known in meteorites and terrestrial objects of different genetic types.

**Keywords:** chladniite, fillowite group, phosphate, crystal structure, fumarolic sublimates, Tolbachik Volcano

**DOI:** 10.1134/S1028334X23601591

Chladniite, a mineral with the idealized formula  $\text{Na}_3\text{CaMg}_{11}[\text{PO}_4]_9$ , belongs to the fillowite group which also includes fillowite  $\text{Na}_3\text{CaMn}_{11}^{2+}[\text{PO}_4]_9$ , johnsomervilleite  $\text{Na}_3\text{CaFe}_{11}^{2+}[\text{PO}_4]_9$ , and galileiite  $\text{Na}_3\text{Fe}^{2+}\text{Fe}_{11}^{2+}[\text{PO}_4]_9$ . All these isostructural phosphates are trigonal. The space group is  $R-3$ ,  $a = 14.9$ – $15.3$  Å, and  $c = 41.7$ – $43.3$  Å [1–8]. This formula record with 36 O atoms per formula ( $Z = 12$ ) was approved by the International Mineralogical Association only in 2021 after the adoption of the new nomenclature of the fillowite group [8]. Initially, chladniite was described in 1994 with the formula  $\text{Na}_2\text{CaMg}_7[\text{PO}_4]_6$  ( $Z = 18$ ) [3]. It should also be noted that stornesite-(Y) characterized in 2006 as a new mineral of the fillowite group with the formula  $(\text{Y,Ca})\square_2\text{Na}_6(\text{Ca,Na})_8(\text{Mg,Fe})_{43}(\text{PO}_4)_{36}$  ( $Z = 3$ ) [6] was assigned to the rare-earth variety of chladniite under the development of this nomenclature and,

accordingly, was discredited as an independent mineral variety [8].

Chladniite was first found in iron [3] and stone [9] meteorites, and then, on the Earth, in metamorphic rocks [6] and in phosphate-rich granitic pegmatites [7, 8]. The chemical composition of chladniite samples from objects of various genesis differs markedly (Table 1).

We discovered a new chladniite variety with an unusual chemical composition in high-temperature fumarole exhalations in the Tolbachik Volcano (Kamchatka), in particular, in the Arsenatnaya fumarole on the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (GTFE) in 1975–1976. This large active oxidizing fumarole, known due to the unique diversity and originality of exhalation minerals, was described, in particular, in terms of mineralogical and geochemical zoning, in [11]. Despite the fact that almost half a century has passed since the end of the GTFE, numerous fumaroles of the Second scoria cone remain active, and the gas temperature, which we regularly measured in the period of 2012–2022, reaches 500°C in them.

Chladniite was found in July 2017 in the deep (about 3 m from the day surface) hottest zone of the Arsenatnaya fumarole, in highly mineralized cavities with a temperature of 450–480°C at the sampling time. This mineral forms colorless, water-transparent,

<sup>a</sup> Moscow State University, Moscow, 119991 Russia

<sup>b</sup> Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, 115162 Russia

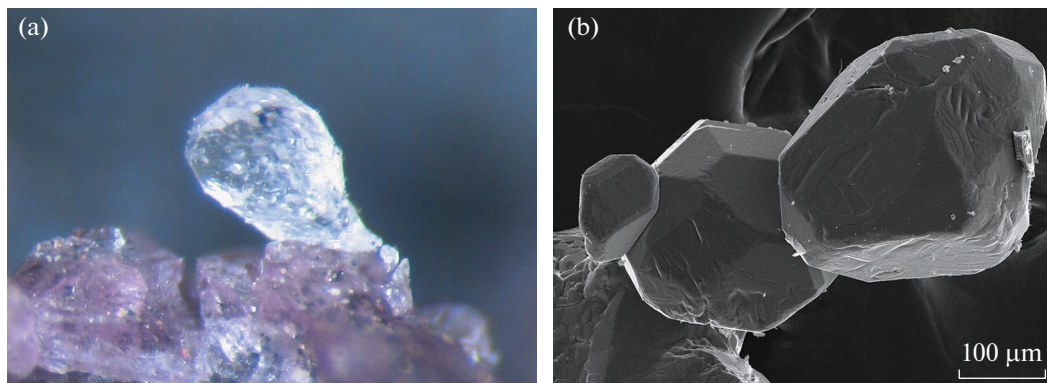
<sup>c</sup> Institute of Volcanology and Seismology, Far East Branch, Russian Academy of Sciences, Petropavlovsk-Kamchatsky, 683000 Russia

\*e-mail: igorpekov@mail.ru

**Table 1.** Chemical composition of chladniite from meteorites (1–3) and terrestrial objects (4–7)

No.	1	2	3	4	5	6	7
wt %							
Na <sub>2</sub> O	6.6	6.75	7.14	5.62	5.53	5.04	6.51 (6.19–6.81)
CaO	6.59	3.87	6.65	5.52	4.88	5.66	6.07 (5.82–6.45)
MgO	33.5	19.8	29.86	11.56	9.42	23.16	33.31 (32.68–33.87)
MnO	0.30	8.61	1.37	14.42	13.96	0.24	1.33 (1.11–1.52)
FeO	2.2	14.4	5.11	17.37	15.98	15.55	–
Fe <sub>2</sub> O <sub>3</sub>					5.53		–
Y <sub>2</sub> O <sub>3</sub>						1.43	–
SiO <sub>2</sub>	0.59	–	0.63			0.02	–
P <sub>2</sub> O <sub>5</sub>	49.9	46.4	48.74	45.29	44.02	48.11	45.54 (44.86–46.65)
As <sub>2</sub> O <sub>5</sub>							7.58 (6.38–8.37)
Total	99.68	99.89*	100.05*	100.15*	99.35*	99.53*	100.34
Number of atoms per formula (a.f.) calculated for 36 oxygen atoms (Z = 12)							
Na	2.67	2.99	2.94	2.59	2.58	2.17	2.67
Ca	1.48	0.95	1.52	1.41	1.26	1.35	1.38
Mg	10.44	6.73	9.47	4.10	3.38	7.68	10.52
Mn	0.05	1.66	0.25	2.90	2.85	0.05	0.24
Fe <sup>2+</sup>	0.38	2.75	0.91	3.45	3.22	2.89	–
Fe <sup>3+</sup>					1.00		–
Y						0.17	–
Si	0.12	–	0.13			–	–
P	8.83	8.96	8.78	9.11	8.97	9.05	8.17
As							0.84
ΣM	15.02	15.09	15.18	14.51	14.30	14.33	14.81
ΣT	8.95	8.96	8.91	9.11	8.97	9.06	9.01

(1) Carlton iron meteorite, Texas, United States [3]; (2) GRA 95209 stony meteorite, East Antarctic region [9]; (3) Elga iron meteorite, Yakutia [10]; (4) Tablada I granite pegmatite, Cordoba, Argentina [7]; (5) Sapucaia granite pegmatite, Minas Gerais, Brazil [8]; (6) paragneiss, Larsemann Hills, East Antarctic region: “stornesite-(Y)” [6]; (7) Arsenatnaya fumarole, Tolbachik Volcano, Kamchatka: our data (average over 13 analyses, scatter in brackets). \*The analysis total also includes, wt %, (2) 0.06 NiO (= 0.01 a.f. Ni); (3) 0.55 TiO<sub>2</sub> (= 0.09 a.f. Ti); (4) 0.37 ZnO (= 0.06 a.f. Zn); (5) 0.01 K<sub>2</sub>O, 0.02 Al<sub>2</sub>O<sub>3</sub> (= 0.01 a.f. Al); (6) 0.02 SrO, 0.24 Yb<sub>2</sub>O<sub>3</sub> (= 0.02 a.f. Yb), 0.01 UO<sub>2</sub>, 0.05 SO<sub>3</sub> (= 0.01 a.f. S). ΣM is the total of all metal cations, ΣT = P + As + Si + S. A dash means that the component content is below the detection limit; an empty cell means no data.



**Fig. 1.** Chladniite crystals from the Arsenatnaya fumarole (Tolbachik): (a) a colorless crystal of 0.5 mm in size with pale lilac cal-ciojohillerite (photo image by I.V. Pektiv and A.V. Kasatkin); (b) intergrowth of crystals (SEM image in SE).

**Table 2.** Crystallographic characteristics, single-crystal experiment data, and parameters of the refinement of the Tolbachik chladniite structure

Formula (from structural data)	Na <sub>10.71</sub> Ca <sub>5.05</sub> Mg <sub>42.18</sub> Mn <sub>1.00</sub> (P <sub>33.53</sub> As <sub>2.47</sub> )O <sub>144</sub>
Formula weight	5056.58
Temperature, K	293(2)
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073
Crystal system, space group, Z	Trigonal, <i>R</i> -3, 3
Unit cell parameters, Å	<i>a</i> = 14.9831(2) <i>c</i> = 42.8050(7)
<i>V</i> , Å <sup>3</sup>	8322.1(3)
Estimated density, g/cm <sup>3</sup>	3.027
Absorption coefficient $\mu$ , mm <sup>-1</sup>	2.037
<i>F</i> <sub>000</sub>	7459
Crystal size, mm	0.10 × 0.11 × 0.13
Absorption correction	Multiscan
$\theta_{\min}/\theta_{\max}$ , deg	2.719/28.282
Index ranges	-19 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 19, -57 ≤ <i>l</i> ≤ 57
Number of measured reflections	48884
Number of independent reflections	4584 ( <i>R</i> <sub>int</sub> = 0.0653)
Number of independent reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4254
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Number of refined parameters	374
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0432, <i>wR</i> 2* = 0.0663
<i>R</i> (for all data)	<i>R</i> 1 = 0.0499, <i>wR</i> 2* = 0.0682
GoF	1.242
$\Delta\rho_{\max}/\Delta\rho_{\min}$ , e/Å <sup>3</sup>	0.80/-0.95

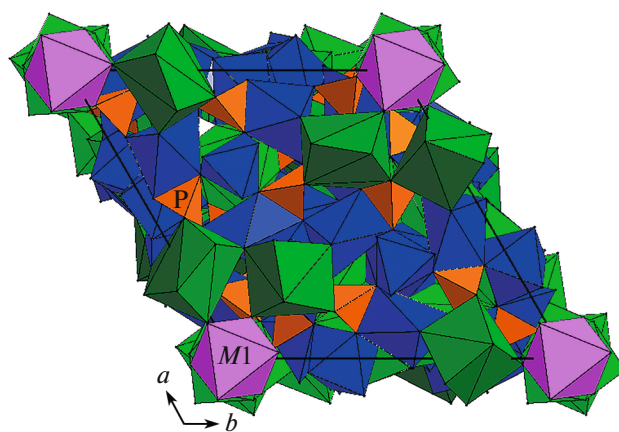
$$*w = 1/[\sigma^2(F_o^2) + (0.0098P)^2 + 58.1670P]; P = \{\max(0 \text{ or } F_o^2) + 2F_c^2\}/3.$$

glassy, isometric, or elongated crystals of up to 0.5 mm in size (Fig. 1a) and skeletal intergrowths of up to 2 mm. Chladniite crystals (symmetry class  $\bar{3}$ ) consist of faces of two hexagonal prisms, several rhombohedra, and a pinacoid. Their degree of perfection varies from relatively clear polyhedrons (Fig. 1b) to coarse, sometimes rounded individuals. They grow on the walls of the cavity composed of basalt slag processed by fumarole gases. In exhalation encrustations, chladniite is closely associated with P-bearing calciojo-hillerite NaCaMg<sub>3</sub>[(As,P)O<sub>4</sub>]<sub>3</sub>, As-bearing fluorapatite Ca<sub>5</sub>[(P,As)O<sub>4</sub>]<sub>3</sub>F, metathénardite, diopside, enstatite, forsterite, and hematite.

The chemical composition of Tolbachik chladniite was determined by the electron probe method with a JEOL 733 microanalyzer at an accelerating voltage of 20 kV and a beam current of 10 nA. Standards: (Na) albite, (Mg) chromite, (Ca) wollastonite, (Mn) Mn, (P) LaPO<sub>4</sub>, and (As) InAs. The contents of other elements with atomic numbers >8 turned out to be below the detection limit. The composition of our sample is given in Table 1 (analysis 7) in comparison with that of chladniite from other objects. All empirical formulas in Table 1 are calculated according to a unified proce-

cedure in accordance with the current nomenclature of the fillowite group [8].

The X-ray study of a single crystal of Tolbachik chladniite was accomplished by means of an Xcalibur



**Fig. 2.** Crystal structure of Tolbachik chladniite. Mg-dominant polyhedra (*M*2–11) are blue, Ca-dominant ones (*M*12) are dark green, and Na-dominant ones (*M*13, *M*21, and *M*31) are light green. A thick black line shows the unit cell.

**Table 3.** Coordinates and equivalent displacement parameters ( $U_{eq}$ , Å<sup>2</sup>) of atoms, occupancy (s.o.f.), and multiplicity ( $Q$ ) of positions in the Tolbachik chladniite structure

Position	$x$	$y$	$z$	$U_{eq}$	s.o.f.	$Q$
M1	0.0	0.0	0.0	0.0019(2)	Mn <sub>1.00</sub>	3
M2	0.0	0.0	0.5	0.0068(7)	Mg <sub>0.54(2)</sub> Ca <sub>0.46(2)</sub>	3
M3	0.0	0.0	0.10402(4)	0.0092(4)	Mg <sub>1.00</sub>	6
M4	0.0	0.0	0.32485(4)	0.0087(3)	Mg <sub>1.00</sub>	6
M5	0.0	0.0	0.39635(4)	0.0097(4)	Mg <sub>1.00</sub>	6
M6	0.43132(8)	0.25383(8)	0.05191(2)	0.0113(2)	Mg <sub>1.00</sub>	18
M7	0.11221(8)	0.57469(9)	0.03883(2)	0.0133(2)	Mg <sub>1.00</sub>	18
M8	0.00275(8)	0.32325(8)	0.08160(2)	0.0079(2)	Mg <sub>1.00</sub>	18
M9	0.25978(8)	0.32750(8)	0.08609(2)	0.0075(2)	Mg <sub>1.00</sub>	18
M10	0.57631(9)	0.08057(8)	0.12418(3)	0.0173(4)	Mg <sub>0.940(9)</sub> Ca <sub>0.060(9)</sub>	18
M11	0.22464(9)	0.11063(9)	0.13516(3)	0.0201(3)	Mg <sub>1.00</sub>	18
M12	0.26710(6)	0.29378(6)	0.00023(2)	0.0141(3)	Ca <sub>0.642(8)</sub> Na <sub>0.358(8)</sub>	18
M13	0.0	0.0	0.17628(9)	0.0134(13)	Na <sub>0.559(10)</sub>	6
M21	0.0	0.0	0.24680(5)	0.0199(8)	Na <sub>0.811(15)</sub> Ca <sub>0.189(15)</sub>	6
M31	0.07871(12)	0.42914(12)	0.16524(3)	0.0215(5)	Na <sub>0.970(6)</sub>	18
P1	0.18953(5)	0.43443(5)	0.02798(2)	0.0041(2)	P <sub>0.959(3)</sub> As <sub>0.041(3)</sub>	18
P2	0.53166(5)	0.11541(5)	0.03808(2)	0.0052(2)	P <sub>0.963(3)</sub> As <sub>0.037(3)</sub>	18
P3	0.54602(5)	0.09218(5)	0.19939(2)	0.0069(2)	P <sub>0.880(3)</sub> As <sub>0.120(3)</sub>	18
P4	0.22049(5)	0.12694(5)	0.21050(2)	0.0082(2)	P <sub>0.918(3)</sub> As <sub>0.082(3)</sub>	18
P5	0.22395(5)	0.46069(5)	0.22280(2)	0.0053(2)	P <sub>0.919(3)</sub> As <sub>0.081(3)</sub>	18
P6	0.46773(5)	0.21493(5)	0.27830(2)	0.0073(2)	P <sub>0.949(3)</sub> As <sub>0.051(3)</sub>	18
O1	0.16194(16)	0.38256(16)	-0.00461(5)	0.0105(4)	O <sub>1.00</sub>	18
O2	0.25342(17)	0.55422(16)	0.02566(5)	0.0127(4)	O <sub>1.00</sub>	18
O3	0.25529(17)	0.39725(17)	0.04559(5)	0.0129(5)	O <sub>1.00</sub>	18
O4	0.08795(16)	0.41008(17)	0.04439(5)	0.0127(5)	O <sub>1.00</sub>	18
O5	0.45555(16)	0.13013(16)	0.05876(5)	0.0123(4)	O <sub>1.00</sub>	18
O6	0.55428(17)	0.03310(17)	0.05076(5)	0.0140(5)	O <sub>1.00</sub>	18
O7	0.63883(16)	0.21713(16)	0.03847(5)	0.0109(4)	O <sub>1.00</sub>	18
O8	0.48914(18)	0.09298(17)	0.00463(5)	0.0145(5)	O <sub>1.00</sub>	18
O9	0.54310(17)	0.03150(17)	0.16981(5)	0.0151(5)	O <sub>1.00</sub>	18
O10	0.63619(17)	0.20551(17)	0.19844(5)	0.0158(5)	O <sub>1.00</sub>	18
O11	0.44108(17)	0.09176(17)	0.20202(5)	0.0136(5)	O <sub>1.00</sub>	18
O12	0.54856(17)	0.03495(17)	0.22982(5)	0.0136(5)	O <sub>1.00</sub>	18
O13	0.2373(2)	0.0844(2)	0.18007(6)	0.0319(7)	O <sub>1.00</sub>	18
O14	0.12780(17)	0.14360(18)	0.20868(6)	0.0180(5)	O <sub>1.00</sub>	18
O15	0.89277(16)	0.23562(16)	0.11435(5)	0.0120(4)	O <sub>1.00</sub>	18
O16	0.19575(18)	0.04031(17)	0.23535(5)	0.0174(5)	O <sub>1.00</sub>	18
O17	0.26663(18)	0.52752(18)	0.19388(5)	0.0175(5)	O <sub>1.00</sub>	18
O18	0.10209(16)	0.39550(17)	0.22111(5)	0.0128(5)	O <sub>1.00</sub>	18
O19	0.25454(17)	0.37565(17)	0.22366(5)	0.0129(5)	O <sub>1.00</sub>	18
O20	0.25269(16)	0.52438(16)	0.25364(5)	0.0112(4)	O <sub>1.00</sub>	18
O21	0.5310(2)	0.2434(2)	0.24820(7)	0.0329(7)	O <sub>1.00</sub>	18
O22	0.37674(16)	0.10017(16)	0.27302(5)	0.0131(5)	O <sub>1.00</sub>	18
O23	0.41992(18)	0.28365(17)	0.28296(5)	0.0153(5)	O <sub>1.00</sub>	18
O24	0.5236(2)	0.2113(2)	0.30744(7)	0.0320(7)	O <sub>1.00</sub>	18

**Table 4.** Selected interatomic distances (Å) in the Tolbachik chladniite structure

<i>M1</i> – O24	2.290(3) × 6	<i>M9</i> – O18	2.002(2)	<i>M31</i> – O9	2.319(3)
		– O22	2.014(2)	– O17	2.460(3)
<i>M2</i> – O17	2.149(2) × 6	– O3	2.042(2)	– O18	2.505(3)
		– O12	2.080(2)	– O19	2.511(3)
<i>M3</i> – O21	1.965(3) × 3	– O11	2.238(2)	– O9	2.516(3)
– O10	2.179(2) × 3			– O11	2.716(3)
		<i>M10</i> – O14	1.977(2)	– O17	2.730(3)
<i>M4</i> – O7	2.031(2) × 3	– O9	2.058(3)		
– O2	2.096(2) × 3	– O16	2.088(3)	<i>P1</i> – O4	1.545(2)
		– O18	2.119(2)	– O3	1.549(2)
<i>M5</i> – O20	1.985(2) × 3	– O19	2.302(3)	– O1	1.549(2)
– O2	2.193(2) × 3	– O13	2.594(3)	– O2	1.559(2)
<i>M6</i> – O22	2.014(2)	<i>M11</i> – O11	1.962(2)	<i>P2</i> – O6	1.532(2)
– O7	2.056(2)	– O13	1.990(3)	– O8	1.535(2)
– O16	2.059(3)	– O15	2.006(2)	– O5	1.544(2)
– O5	2.080(2)	– O10	2.019(3)	– O7	1.567(2)
– O1	2.125(2)	– O21	2.459(3)		
– O6	2.594(2)			<i>P3</i> – O9	1.547(2)
		<i>M12</i> – O23	2.356(2)	– O10	1.554(2)
<i>M7</i> – O8	1.965(2)	– O1	2.475(2)	– O12	1.570(2)
– O6	1.974(2)	– O1	2.528(2)	– O11	1.573(2)
– O20	2.031(2)	– O3	2.546(2)		
– O4	2.319(2)	– O24	2.550(3)	<i>P4</i> O13	1.525(3)
– O2	2.353(2)	– O8	2.586(2)	<i>P4</i> O14	1.531(2)
– O3	2.374(3)	– O4	2.740(2)	<i>P4</i> O15	1.561(2)
		– O22	2.805(2)	<i>P4</i> O16	1.572(2)
<i>M8</i> – O4	2.049(2)	<i>M13</i> – O14	2.470(3) × 3	<i>P5</i> O17	1.518(2)
– O15	2.059(2)	– O10	2.478(4) × 3	<i>P5</i> O19	1.555(2)
– O23	2.120(2)			<i>P5</i> O20	1.558(2)
– O19	2.120(2)	<i>M21</i> – O7	2.591(3) × 3	<i>P5</i> O18	1.584(2)
– O12	2.157(2)	– O14	2.615(3) × 3		
– O5	2.233(2)	– O16	2.727(2) × 3	<i>P6</i> O24	1.518(3)
				<i>P6</i> O21	1.529(3)
				<i>P6</i> O23	1.533(2)
				<i>P6</i> O22	1.588(2)

S CCD diffractometer for a full sphere of reciprocal space. The crystal structure of the mineral was determined and refined using SHELX software package [12] with the fillowite structural model [2] as the initial one. The crystallographic characteristics, single-crystal experiment data, and structure refinement parameters are given in Table 2; the atomic coordinates, atomic displacement parameters, site multiplicity, and site occupancy factors are in Table 3; and the inter-

atomic distances, in Table 4. Atomic positions are denoted by the letters *M* (metal cations), *P* (tetrahedrally coordinated components), and *O* (oxygen atoms), according to [8]. The crystallochemical formula ( $Z = 3$ ) was obtained based on the structure refinement results:  $M^{13}(\text{Na}_{0.56}\square_{0.44})_2^{M^{21}}(\text{Na}_{0.81}\text{Ca}_{0.19})_2^{M^{31}}(\text{Na}_{0.97}\square_{0.03})_6^{M^{12}}(\text{Ca}_{0.64}\text{Na}_{0.36})_6^{M^1}\text{Mn}^{M^2}(\text{Mg}_{0.54}\text{Ca}_{0.46})^{M^{3-9}}\text{Mg}_{30}^{M^{10}}(\text{Mg}_{0.94}\text{Ca}_{0.06})_6^{M^{11}}\text{Mg}_6(\text{P}_{33.53}\text{As}_{2.47})\text{O}_{144}$ . It

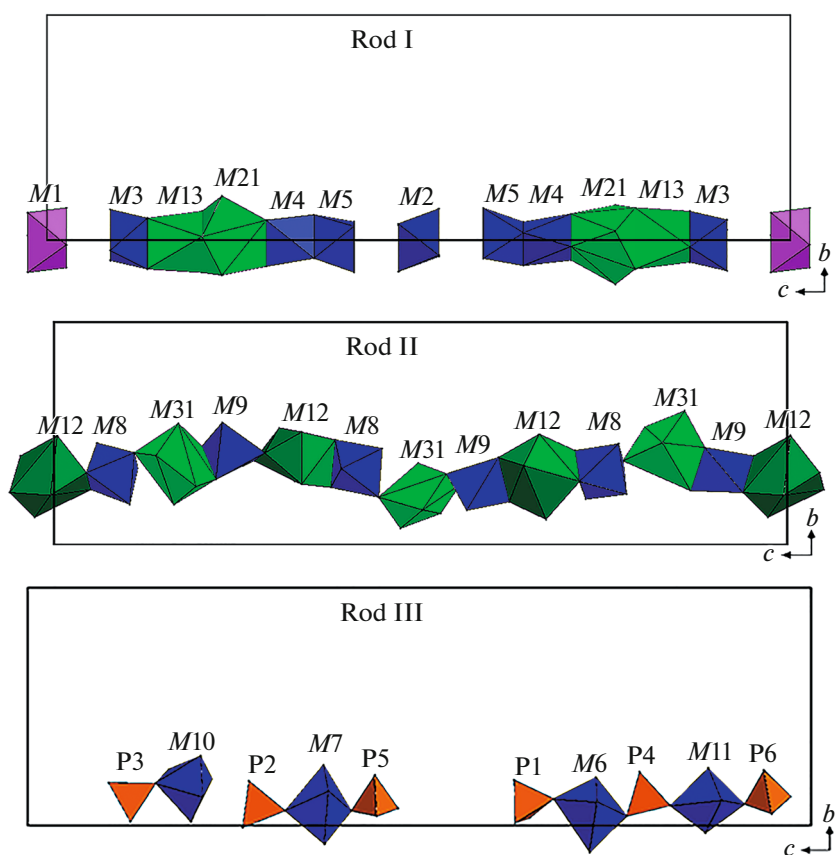


Fig. 3. Polyhedral rods in the chladniite structure.

is in good agreement with the electron microprobe data (Table 1, analysis 7).

The atomic structure of chladniite (Fig. 2) is topologically identical to that of other members of the fillowite group. The differences between them are in the nature and degree of site occupancy, as well as in the configuration of *M*-centered polyhedra. The structural features of fillowite-like compounds are detailed in [2] using the hexagonal mosaic pattern of polyhedral rods proposed by P.B. Moore [13]. Three types of rods extended along the axis *c* (I, II, and III) built by polyhedra of *M*-cations and  $\text{PO}_4$  tetrahedra are distinguished in these structures; rods I and III are broken and contain vacancies (Fig. 3). As in other structurally studied samples of fillowite group minerals, in Tolbachik chladniite, rod I consists of connected *via* common faces *M*-polyhedra and vacancies ( $\square$ ) in the sequence  $^{\text{VI}}\text{M1}-\square-^{\text{VI}}\text{M3}-^{\text{VI}}\text{M13}-^{\text{IX}}\text{M21}-^{\text{VI}}\text{M4}-^{\text{VI}}\text{M5}-\square-^{\text{VI}}\text{M2}-\square-^{\text{VI}}\text{M5}-^{\text{VI}}\text{M4}-^{\text{IX}}\text{M21}-^{\text{VI}}\text{M13}-^{\text{VI}}\text{M3}-\square$  (Ro-man numerals denote the coordination numbers of *M*-cations). Rod II consists of *M*-polyhedra connected *via* common edges and vertices as  $^{\text{VIII}}\text{M12}-^{\text{V}}\text{M9}-^{\text{VII}}\text{M31}-^{\text{VI}}\text{M8}-^{\text{VIII}}\text{M12}-^{\text{V}}\text{M9}-^{\text{VII}}\text{M31}-^{\text{VI}}\text{M8}-^{\text{VIII}}\text{M12}-^{\text{V}}\text{M9}-^{\text{VII}}\text{M31}-^{\text{VI}}\text{M8}$ . Rod III combines (P,As) $\text{O}_4$  tetrahedra (it includes all six crystallographically non-

equivalent P tetrahedra: Table 3), *M*-polyhedra, and vacancies in the sequence  $\text{P6}-^{\text{V}}\text{M11}-\text{P4}-^{\text{VI}}\text{M6}-\text{P1}-\square-\text{P5}-^{\text{VI}}\text{M7}-\text{P2}-\square-^{\text{VI}}\text{M10}-\text{P3}-\square$ .

Structures of four chladniite samples were studied earlier [4, 6–8]. They represent various chemical chladniite varieties which correspond in composition to analyses 1, 4, 5, and 6 in Table 1. Table 5 reports the comparative data on the occupancy of *M*-positions in all five structurally studied chladniite samples. It makes no sense to compare the occupancy of P sites, because this information is given for our sample in Table 3. As for all previously studied samples, the P-positions are occupied, in fact, by phosphorus atoms alone. According to Table 5, large cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{REE}^{3+}$ , and the largest of the medium-sized cations  $\text{Mn}^{2+}$ ) are concentrated primarily in the positions *M31*, *M21*, *M12*, *M13*, and *M1*; the *M13* polyhedron shows a clear trend towards the availability of vacancies. An exception is, to some extent, a sample from Sapucaia granite pegmatite in Brazil [8], where positions *M13* and *M1*, on the contrary, are dominated by the smallest cation  $\text{Mg}^{2+}$ , while *M4* is dominated by large  $\text{Na}^+$ . This inversion can be due to the structure distortion as a result of the unusually high total of Fe and Mn that occurs in the mineral. In the *M2*–*11*

**Table 5.** Distribution of cations over *M*-positions in the structurally studied chladniite samples from different objects

Position	Carlton meteorite, Texas, United States*	Paragneiss, Larsemann Hills, East Antarctic region	Tablada I granite pegmatite, Cordoba, Argentina	Sapucaia granite pegmatite, Minas Gerais, Brazil	Arsenatnaya fumarole, Tolbachik Volcano, Kamchatka
<i>M1</i>	Ca <sub>1.00</sub>	Y <sub>0.68</sub> Ca <sub>0.26</sub> Yb <sub>0.06</sub>	Mn <sub>0.59</sub> Fe <sub>0.20</sub> <sup>2+</sup> Ca <sub>0.18</sub> Mg <sub>0.03</sub>	Mg <sub>0.60</sub> Mn <sub>0.40</sub>	Mn <sub>1.00</sub>
<i>M2</i>	Mg <sub>1.00</sub>	Fe <sub>0.51</sub> <sup>2+</sup> Mg <sub>0.49</sub>	Mg <sub>0.80</sub> Mn <sub>0.11</sub> Ca <sub>0.09</sub>	Mn <sub>0.54</sub> Fe <sub>0.46</sub> <sup>2+</sup>	Mg <sub>0.54</sub> Ca <sub>0.46</sub>
<i>M3</i>	Mg <sub>1.00</sub>	Mg <sub>0.97</sub> Fe <sub>0.03</sub> <sup>2+</sup>	Mg <sub>0.94</sub> Fe <sub>0.06</sub> <sup>2+</sup>	Mg <sub>0.90</sub> Fe <sub>0.10</sub> <sup>2+</sup>	Mg <sub>1.00</sub>
<i>M4</i>	Mg <sub>1.00</sub>	Mg <sub>0.97</sub> Fe <sub>0.03</sub> <sup>2+</sup>	Mg <sub>0.92</sub> Fe <sub>0.08</sub> <sup>3+</sup>	Na <sub>0.90</sub> □ <sub>0.10</sub>	Mg <sub>1.00</sub>
<i>M5</i>	Mg <sub>1.00</sub>	Mg <sub>1.00</sub>	Mg <sub>0.96</sub> Ca <sub>0.04</sub>	Mg <sub>0.70</sub> Fe <sub>0.30</sub> <sup>3+</sup>	Mg <sub>1.00</sub>
<i>M6</i>	Mg <sub>1.00</sub>	Mg <sub>0.72</sub> Fe <sub>0.28</sub> <sup>2+</sup>	Fe <sub>0.50</sub> <sup>2+</sup> Mg <sub>0.40</sub> Fe <sub>0.10</sub> <sup>3+</sup>	Fe <sub>0.60</sub> <sup>2+</sup> Mg <sub>0.20</sub> Ca <sub>0.20</sub>	Mg <sub>1.00</sub>
<i>M7</i>	Mg <sub>1.00</sub>	Mg <sub>0.545</sub> Fe <sub>0.455</sub> <sup>2+</sup>	Mn <sub>0.69</sub> Ca <sub>0.15</sub> Mg <sub>0.12</sub> Zn <sub>0.04</sub>	Mn <sub>0.50</sub> Mg <sub>0.40</sub> Fe <sub>0.10</sub> <sup>2+</sup>	Mg <sub>1.00</sub>
<i>M8</i>	Mg <sub>1.00</sub>	Mg <sub>0.89</sub> Fe <sub>0.11</sub> <sup>2+</sup>	Mg <sub>0.56</sub> Mn <sub>0.37</sub> Ca <sub>0.07</sub>	Mg <sub>0.50</sub> Fe <sub>0.50</sub> <sup>2+</sup>	Mg <sub>1.00</sub>
<i>M9</i>	Mg <sub>1.00</sub>	Mg <sub>0.63</sub> Fe <sub>0.37</sub> <sup>2+</sup>	Fe <sub>0.46</sub> <sup>2+</sup> Mg <sub>0.30</sub> Fe <sub>0.20</sub> <sup>3+</sup> Mn <sub>0.04</sub>	Mn <sub>0.50</sub> Fe <sub>0.30</sub> <sup>2+</sup> Mg <sub>0.20</sub>	Mg <sub>1.00</sub>
<i>M10</i>	Mg <sub>1.00</sub>	Mg <sub>0.79</sub> Fe <sub>0.21</sub> <sup>2+</sup>	Mn <sub>0.68</sub> Fe <sub>0.20</sub> <sup>2+</sup> □ <sub>0.12</sub>	Mn <sub>0.80</sub> Mg <sub>0.20</sub>	Mg <sub>0.94</sub> Ca <sub>0.06</sub>
<i>M11</i>	Mg <sub>1.00</sub>	Mg <sub>0.67</sub> Fe <sub>0.33</sub> <sup>2+</sup>	Fe <sub>0.71</sub> <sup>2+</sup> Mg <sub>0.29</sub>	Fe <sub>0.60</sub> <sup>2+</sup> Na <sub>0.20</sub> Fe <sub>0.10</sub> <sup>3+</sup> Ca <sub>0.10</sub>	Mg <sub>1.00</sub>
<i>M12</i>	Ca <sub>0.69</sub> Na <sub>0.31</sub>	Ca <sub>0.58</sub> Na <sub>0.42</sub>	Ca <sub>0.65</sub> Na <sub>0.35</sub>	Na <sub>1.00</sub>	Ca <sub>0.64</sub> Na <sub>0.36</sub>
<i>M13</i>	Na <sub>0.81</sub> □ <sub>0.19</sub>	□ <sub>0.94</sub> Na <sub>0.06</sub>	□ <sub>0.52</sub> Na <sub>0.48</sub>	Mg <sub>0.60</sub> Fe <sub>0.40</sub> <sup>3+</sup>	Na <sub>0.56</sub> □ <sub>0.44</sub>
<i>M21</i>	Na <sub>1.00</sub>	Ca <sub>0.68</sub> Na <sub>0.32</sub>	Na <sub>0.60</sub> Mn <sub>0.25</sub> □ <sub>0.15</sub>	Na <sub>0.90</sub> Ca <sub>0.10</sub>	Na <sub>0.81</sub> Ca <sub>0.19</sub>
<i>M31</i>	Na <sub>1.00</sub>	Na <sub>1.00</sub>	Na <sub>0.98</sub> □ <sub>0.02</sub>	Ca <sub>0.50</sub> □ <sub>0.35</sub> Fe <sub>0.15</sub> <sup>3+</sup>	Na <sub>0.97</sub> □ <sub>0.03</sub>
Reference	[4]	[6]	[7]	[8]	Our data

(\*) When refining the structure, the major Fe impurity (Table 1) was ignored by the authors of [4]. Judging from the atomic displacement parameters given in this work, Fe is likely included in *M2* and, to a lesser extent, in *M9*, *M5*, and *M7*.

group, *M2*, *M6*–*7*, and *M9*–*11* can be considered the most isomorphically capacious with respect to cations larger than Mg<sup>2+</sup>.

Table 1 shows two basic individual features of the chemical composition of Tolbachik fumarolic chladniite such as the substantial enrichment in As replacing P and the absence of Fe. Hence, a new Fe-free As-bearing mineral variety can be identified. It should be noted that in terms of metal cations (*M*), our sample is closer to the ideal formula of Na<sub>3</sub>CaMg<sub>11</sub>[PO<sub>4</sub>]<sub>9</sub> than chladniite from all objects previously known for this mineral: the total content of impurities in *M*-positions (i.e., any *M*-cations, except Na, Ca, and Mg) in it is the lowest. These impurities are represented in Tolbachik chladniite only by Mn (1.3 wt % MnO) separated in the *M1*-position (Tables 1, 3, 5).

A considerable isomorphism between P<sup>5+</sup> and As<sup>5+</sup> is characteristic of many minerals in the high-temperature parageneses of the oxidation-type Tolbachik fumaroles. It was recorded in representatives of the

apatite, titanite, and wagnerite structural types [14]. In our case, it is interesting to compare the P and As distribution between closely associated (Fig. 1a) and, judging from their relationship, simultaneously crystallized P-bearing arsenate calciojohillerite NaCaMg<sub>3</sub>[(As,P)O<sub>4</sub>]<sub>3</sub> and As-containing phosphate chladniite Na<sub>3</sub>CaMg<sub>11</sub>[(P,As)O<sub>4</sub>]<sub>9</sub>. These oxosalts have the same set of metal cations, but the former belongs to the alluaudite structural type [15], and the latter, to fillowite. Their paragenesis is clearly indicative of the relative affinity of these structural types for As and P, respectively.

Tolbachik chladniite is interesting not only for its unusual chemical features and the fact that the largest segregations of this mineral were found in this area, but also that well-faceted crystals were found for the first time. In general, volcanic exhalations are a new genetic type for fillowite group minerals which were previously found only in meteorites (all members of the group), granitic pegmatites (fillowite, johnsommer-



villeite, and Fe–Mn-varieties of chladniite), and metamorphic rocks (johnsomervilleite and the Fe–REE variety of chladniite). The Tolbachik oxidation-type fumaroles are characterized by a combination of high temperature and oxygen fugacity with atmospheric pressure. According to [11], the minerals were crystallized in the temperature range of 500–750°C in the zone where chladniite was found. It was the oxidation environment that affected the basic individual features of the mineral from this object: a high As<sup>5+</sup> content and “a sterility” with respect to Fe, in contrast to all other objects, both terrestrial and extraterrestrial, where Fe<sup>2+</sup> is a major impurity component in this phosphate (Table 1). Almost all iron in fumarolic incrustations containing chladniite is concentrated in hematite. Alongside with that, manganese is divalent in chladniite, as is clearly indicated by the M1–O interatomic distances (Table 4); hence, this environment should not be called extremely oxidizing. It should be noted that a technogenic analogue of galileite Na<sub>3</sub>Fe<sub>12</sub><sup>2+</sup>(PO<sub>4</sub>)<sub>9</sub> [16], the fillowite group member the most enriched in Fe<sup>2+</sup>, was formed at close *PT* parameters, but in a highly reducing environment, in the burning dump of a coal mine in Kopeisk (Southern Urals).

In general, the chladniite composition clearly records the chemistry of the mineral-forming system, as already noted in [7], albeit with a less representative material than the current one. Samples from granitic pegmatites are the most enriched in both Fe and Mn; samples from metamorphic rocks are enriched in Fe and REE (Y), but depleted in Mn. Meteorites contain a high-Mg and still elevated-Fe (and in stony ones, also enriched in Mn) variety, while chladniite crystallized in the oxidation-type fumarole system is completely devoid of Fe, but contains As<sup>5+</sup> (Table 1).

#### FUNDING

This work was supported by the Russian Science Foundation, grant no. 19-17-00050.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or

format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

#### REFERENCES

1. A. Livingstone, *Mineral. Mag.* **43**, 833–836 (1980).
2. T. Araki and P. B. Moore, *Am. Mineral.* **66**, 827–842 (1981).
3. T. J. McCoy, I. M. Steele, K. Keil, B. F. Leonard, and M. Endreb, *Am. Mineral.* **79**, 375–380 (1994).
4. I. M. Steele, in *Proc. 25th Lunar and Planetary Science Conf. (LPSC XXV)* (Houston, 1994), pp. 1337–1338.
5. E. J. Olsen and I. M. Steele, *Meteorit. Planet. Sci.* **32**, A155–A156 (1997).
6. E. Grew, Th. Armbruster, O. Medenbach, M. G. Yates, and C. J. Carson, *Am. Mineral.* **91**, 1412–1424 (2006).
7. O. Vallcorba, L. Casas, F. Colombo, C. Frontera, and J. Rius, *Eur. J. Mineral.* **29**, 287–293 (2017).
8. F. Hatert, E. S. Grew, P. Vignola, N. Rotiroli, F. Nestola, P. Keller, M. Baijot, Y. Bruni, A.-M. Franolet, F. Dal Bo, and M. Depret, *Can. Mineral.* **59**, 781–796 (2021).
9. C. Floss, *Am. Mineral.* **84**, 1354–1359 (1999).
10. K. D. Litasov and N. M. Podgornykh, *J. Raman Spectrosc.* **48**, 1518–1527 (2017).
11. I. V. Pekov, N. N. Koshlyakova, N. V. Zubkova, I. S. Lykova, S. N. Britvin, V. O. Yapaskurt, A. A. Agakhanov, N. V. Shchিপalkina, A. G. Turchkova, and E. G. Sidorov, *Eur. J. Mineral.* **30**, 305–322 (2018).
12. G. M. Sheldrick, *Acta Crystallogr. C* **71**, 3–8 (2015).
13. P. B. Moore, *Bull. Mineral.* **104**, 536–547 (1981).
14. N. N. Koshlyakova, I. V. Pekov, M. F. Vigasina, A. A. Agakhanov, and M. A. Nazarova, *Dokl. Earth Sci.* **507** (1), 900–904 (2022).
15. F. Hatert, *Eur. J. Mineral.* **31**, 807–822 (2019).
16. V. V. Sharygin, in *Mineralogy of Technogenesis* (Miass, 2016), pp. 34–54 [in Russian].

*Translated by E. Maslennikova*

**Publisher's Note.** Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.